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Vanadium carbide by MOCVD for mitigating the fuel cladding chemical interaction

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HIGHLIGHTS

- An innovative Metal-Organic Chemical Vapor Deposition setup for VC in the surface of cladding was built.
- The kinetics (temperature, time) of the coating experiment was investigated by using HT9 rectangular cladding samples.
- High temperature diffusion couple test proved the coating can effectively mitigating FCCI.

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ABSTRACT

In this work, a low temperature coating process using an organometallic precursor, vanadocene Cp_2V ($Cp = C_5H_5$) was developed. An innovative coating setup was built to deposit a uniform vanadium carbide layer. The substrate temperature dependence of coating was investigated with different temperatures at 200 °C, 400 °C and 650 °C. Cross section profile and phase identification showed an average thickness of 4 μm VC coating obtained for the sample prepared at 650 °C. Diffusion couples of HT9/VC/Ce was annealed to a temperature of 660 °C for 100 h and compared to the diffusion behavior of uncoated HT9/Ce. The coated diffusion couple showed a substantial decrease inter-diffusion zone. These preliminary results advocate that VC coatings may be feasible as diffusion barriers against Ce and possibly other lanthanide fission products.

1. Introduction

Advanced fast reactors as Sodium-Cooled Fast Reactor (SFR) and Lead-Cooled Fast Reactors (LFR) have been considered for transmutation of spent nuclear fuel. Because of the high dpa (displacements per atom) and temperatures encountered in these reactors, high conductivity metallic uranium-based fuels and ferritic-martensitic steel claddings have been selected. One of the significant challenges with this type of fuel-cladding combination is the inter-diffusion between the fuel and cladding material, particularly at the intended high burn up levels. This phenomenon known as fuel cladding chemical interaction (FCCI) [1] can lead to the formation of lower melting point compounds at the fuel-cladding interface and a loss in effective thickness of the cladding wall, which can eventually result in the changes in heat transfer characteristics and the failure of cladding with further breach of fuel into the coolant.

To mitigate the FCCI, one possible way is to place a physical barrier between the fuel and cladding. The barrier material would have to be less susceptible to interaction at both the fuel and cladding interfaces. In the past decades, diffusion barrier foil [2], electrophoretic deposition (EPD) [3] and lined duplex tubes drawing [4] have been conducted to achieve this goal. But either high temperature processing or limitation on high aspect ratio geometry of long and thin cladding tube restricts their practical application. As high temperature processing can significantly promotes the decarburization and decomposition of martensitic microstructure of cladding materials [5]

The diffusion couple experiments performed by Keiser et al. [6,7] at 700 °C using a cast U-based alloy with added fission products show that both V and Zr appear to be good candidate materials to serve as barriers to FCCI in metallic fuels, while the V diffusion couple has an interdiffusion zone of around 10 μm, which is twelve times less than that of fuel/Zr couple. It has been speculated that vanadium carbide could function effectively as a FCCI barrier. The decarburization of the cladding could potentially be eliminated since the pre-existing carbon in vanadium carbide would limit the

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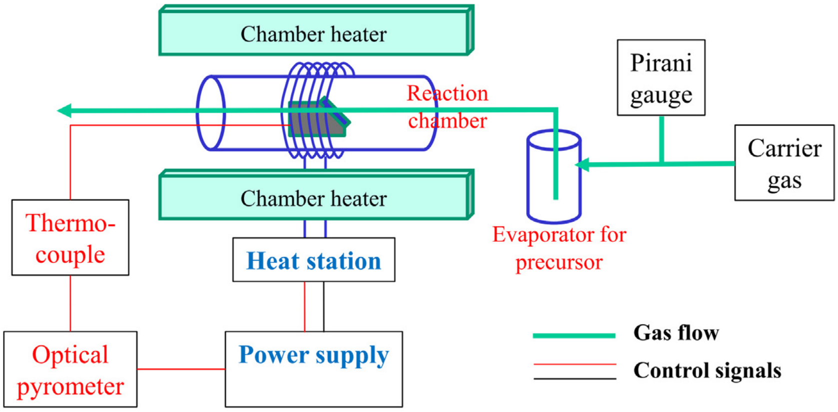

Fig. 1. The system integration diagram for signaling and controlling of the MOCVD setup.

diffusion of carbon from martensitic substrate into coating layer. At the operating temperature and oxygen partial pressure of metal fuel in a SFR, vanadium carbide is stable from aggressive oxidation and can inhibit the steel claddings from scavenging oxygen. Our preliminary study using a pack cementation diffusion coating (PCDC) technique [8] shows that a thin vanadium rich layer, which was lately proved to be vanadium carbide (V_2C), can be successfully deposited on the inner wall of the cladding tube. The diffusion couple experiments between cerium and coated/uncoated HT-9 steels demonstrate that vanadium carbide is effective for mitigating the FCCI. Unfortunately, this pack cementation coating method can only work in practice at a temperature above 730 °C and a growth rate of less than 0.1 μm/hour. Other chemical vapor deposition techniques (CVD, LCVD or PCVD) commonly used for producing vanadium carbide from a gas mixture of hydrogen, methane and vanadium chloride also generally require a high processing temperature (800–1200 °C).

In this study, a low temperature coating process using organometallic precursor, vanadocene Cp_2V ($Cp = C_5H_5$) was developed. A metal organic chemical vapor deposition (MOCVD) setup has been built to deposit a uniform nanostructured vanadium carbide layer on cladding steel. Coating experiment with different substrate temperatures and related characterization of the deposited coating were conducted. To evaluate the efficacy of the coatings for FCCI mitigation, diffusion couple tests were performed with cerium as surrogate for uranium against both the steel and the coatings. As a nonradioactive material, cerium has been widely used as stand-ins for transuranic element, e.g. plutonium, and it is also one of the major lanthanide fission products that diffuse from fuel into the cladding when a steady state FCCI formed.

2. Experimental

To perform the coating experiment, a MOCVD setup has been built as the system diagram shown in Fig. 1.

The kinetics (temperature, time) of the coating experiment was investigated by using HT9 rectangular samples (2mm × 10mm × 15 mm). Prior to the coating experiment, the sample surface was grinded (grits #2000) and polished (5% Perchloric acid + 95% Methanol), which minimizes the factors of surface roughness and oxidation. Sample was placed in a tubular quartz chamber, while the metal-organic precursor taken by carrier gas (hydrogen) flowed through the sample surface. A RF induction heater was applied to increase the substrate temperature using eddy current heating. The temperature measured by thermocouples directly attached to the sample surface provided a feedback signal to control the RF heater, to maintain a constant temperature in the heated zone.

During the deposition process, the precursor temperature was maintained at 110 °C. And to avoid condensation of precursor vapor onto the chamber wall before reaching the HT9 sample, the temperature of chamber segment between the HT9 sample and precursor feeder is maintained at 150 °C. The chamber pressure was kept at around 133 Pa, while the flow rate of carrier gas is suggested to be at least 300 sccm (standard cubic centimeter per minute). In addition, the sample placed in the chamber was tilted 45° to the gas flow direction in order to improve the precursor delivery to the surface and to obtain a uniform coating [2]. The cross-sectional sample was prepared with Focus Ion Beam (FIB – FEI STRATA DB235 DUAL BEAM). To determine the thickness, the ion beam milling at 45° to the surface was used to produce a clean cross-section cut without damaging the coating edge, as shown in Fig. 4. Scan Electron

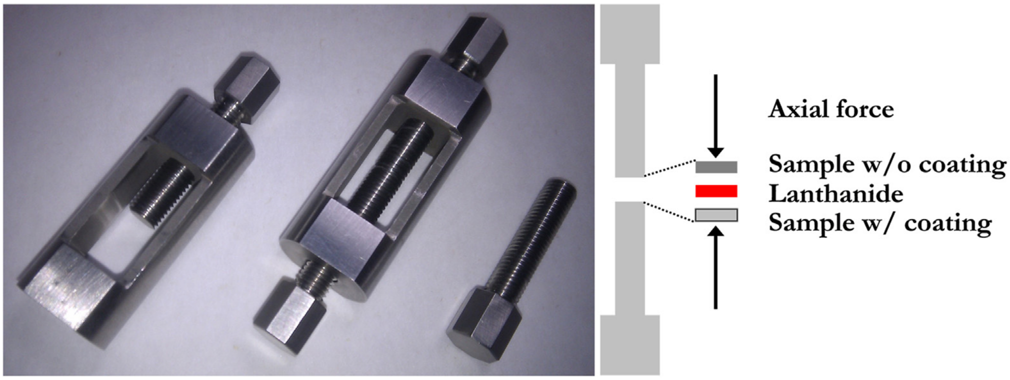

Fig. 2. Diffusion couple assembly made of Kovar alloy and the schematics for experimental.

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