POLYCRYSTALLINE DIAMOND AS PROTECTION OF NUCLEAR FUEL CLADDING AGAINST HIGH TEMPERATURE OXIDATION

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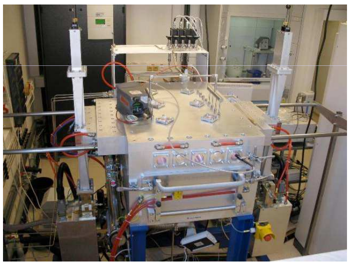
ABSTRACT

Zirconium based alloys are used in almost all types of nuclear reactors as cladding of nuclear fuel, separating fuel from cooling water. During LOCA accidents (when the temperature of coating exceed 800°C) intense heat and pressure triggers a reaction between Zircaloy cladding and the surrounding water steam. The high temperature oxidation of zirconium is accompanied by hydrogen and heat production and can lead up to the degradation of coating and than to the contamination of the primary circuit by fission products. A solution to the problem is to cover the surface with a thin film of a protective substance. Recently, many materials were applied to protect Zircaloy surfaces from destruction, but without any significant success. Nowadays polycrystalline diamond (PCD) films are one of the most promising possibilities how to prevent the nuclear fuel cladding from expansion of high temperature oxidation.

COATING

Diamond withstands very high temperatures, it has excellent thermal conductivity and low chemical reactivity, it does not degrade over time and being pure carbon, it has perfect neutron cross-section properties. Moreover, polycrystalline diamond layers consisting of crystalline (sp3) and amorphous (sp2) carbon phases could have suitable thermal expansion.

Zircaloy2 samples were covered by polycrystalline diamond (PCD) layers in our uniquely constructed Plasma Enhanced Linear Antennas Microwave Chemical Vapor Deposition (PELAMWCVD) system reactor at Institute of Physics Czech Academy of Science. The PELAMWCVD apparatus is capable of producing both continuous wave and tunable pulsed microwaves. The growth chamber potentially allows the deposition on substrates up to the size of 500mm×300mm.

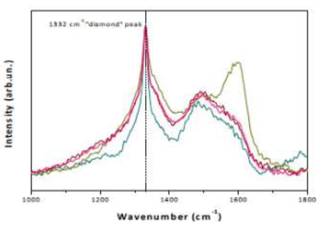


PELAMWCVD reactor

All Zircaloy2 samples were immersed in diamond dispersion with nanodiamond seeds in order to induce nucleation sites at the surface. Samples were placed on a sample holder enabling the full exposure of Zr samples surface to plasma, resulting in spatial diamond growth on the entire surface.

Zircaloy coated by PCD layer

Raman spectroscopy measurements of Zircaloy2 sample coated with the PCD film revealed existence of peaks related to sp3 diamond (1332 cm-1) and sp2 – containing graphitic carbon (1600 cm-1) phases. Measurements were taken at positions over the entire surface of the cladding rod. Both diamond growth and incorporation of amorphous carbon and graphite were detected.



Raman spectra of the Zircaloy coated with the PCD film

TESTING

Characterizations were done for samples of Zircaloy2 covered with diamond layer *before* and *after* both corrosion testing methods - reactor irradiation tests and hot steam oxidation.

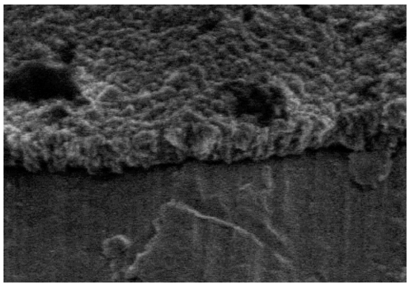
Irradiation Tests

Ion beam irradiation tests of Zircaloy2 samples covered by PCD layers were done at Texas A&M University (TAMU). Irradiation tests were performed in order to mimic the indwelling of nuclear fuel Zircaloy2 cladding under constant neutron bombardment. The PCD coated Zircaloy samples were irradiated by Fe ions of 3 MeV at room temperature. To achieve a damage level of 10 dpa, the sample was irradiated by 3 MeV Fe ions to a fluence of 14 1.95×1016 cm-2. The simulation considered normal incidence of the Fe ions into a flat surface. In reality, the cylindrical surface of t he sample will lead to variance of incidence angles. We therefore characterized the sample region locally normal to the ion beams.

The irradiation was performed at room temperature that is different from working power reactor environments. The projected range of Fe ions is about 1.1 micron and the NCD film thickness is about 300 nm. Therefore Fe ion penetration is deep enough to pass through the NCD/Zircaloy2 interface.

Hot Steam Oxidation

PCD coated Zircaloy sample was exposed in hot steam, at temperature 1100 °C, for 30 minutes. Than the sample was quenched into mixture ice-water. Argon was used as inert atmosphere during steam exposition.



SEM images of polycrystalline diamond layer on the Zircaloy2 rod

CONCLUSION

Overall, we have demonstrated the growth of polycrystalline diamond films on Zr cladding materials and characterized the films before and after ion irradiations. Raman analysis confirm the growth of the PCD film on Zircaloy2. After 3 MeV Fe ion irradiation up to 10 dpa, the PCD film shows satisfactory structural integrity, although Raman suggests partial sp3 (crystalline diamond) to sp2 (amorphous carbon/not graphitic) transition. Ion beam irradiation lowered sp3 phase and increased the sp2 phase content in the layer. After performing the hot steam oxidation tests the diamond layer transformed into thicker amorphous carbon/graphite layer with the substantial content of oxygen inclusion and surface was protected.. The proposed technique is promising for applications in nuclear reactor by increasing accident tolerance of fuel cladding materials.

AKNOWLEDGEMENTS

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