Nanocrystalline diamond protects Zr cladding surface against oxygen and hydrogen uptake: Nuclear fuel durability enhancement

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Abstract

We demonstrate a new strategy for the protection of ZIRLO and Zircaloy 2 nuclear fuel cladding surface by composite polycrystalline diamond (PCD) layers against corrosion in water-cooled nuclear reactors. We show that ZIRLO and Zircaloy 2 fuel cladding samples can be effectively protected against oxygen and hydrogen uptake at both accident and working temperatures in water-cooled nuclear reactor environments by coating the ZIRLO and Zircaloy 2 surface with PCD layers grown in a microwave plasma chemical vapour deposition apparatus. Oxidation of PCD-coated Zr alloy surfaces after more than 100 days in 360 °C hot water was significantly decreased (35-55%) compared with that of unprotected ZIRLO processed under the same conditions. Also at high temperatures (1100 °C), i.e. accident conditions, PCD layers may serve as passive elements for nuclear safety. PCD-protected Zircaloy 2 also exhibited lower hydrogen concentrations than unprotected samples under all investigated conditions; in particular at accident conditions. After ion beam irradiation (10 dpa, 3 MeV Fe2+) PCD layers show satisfactory structural integrity. Protective PCD layers may prolong the lifetime of nuclear cladding and consequently enhance nuclear fuel burnup. PCD layers can also serve as a passive element for nuclear safety. PCD-coated ZIRLO claddings have been selected as a candidate for Accident Tolerant Fuel in commercially operated reactors in 2020.

1.Introduction

Currently, zirconium (Zr) alloys are utilized in all commercially operated power producing light-water (PWR, BWR and VVER) and heavy-water (CANDU) nuclear reactors [1-2]. Generally, Zr alloys surfaces reacts with hot water and hot water steam [3-6]. During this reaction water molecules are dissociated and both oxygen and hydrogen ions penetrate into the Zr alloy[2, 7]. Zr alloys changed by oxygen/hydrogen diffusion are less dense and are mechanically weaker than the original material - their formation results in blistering and finally cracking of the cladding. Oxygen and hydrogen uptake into the Zr alloy change the mechanical properties of the core components and are an important criteria for licensing of nuclear fuel[8-11]. Temperature is the most important factor affecting Zr alloy corrosion - reaction kinetics increases with increasing temperature. Other influencing factors are: exposure time of hot Zr alloy in air, the initial

oxidation of the Zr alloy and the presence of other materials in the melting core. Recently intense heat and pressure triggered a reaction between the nuclear fuel Zr alloy cladding and the surrounding water steam producing explosive hydrogen gas, and several hydrogen-air chemical explosions occurred (Fukushima-Daichi nuclear power plant disaster, Three Mile Island nuclear power station accident)[2, 11-12].

Due to possibility of hydrogen-air chemical explosions the concept of accident-tolerant fuels has been proposed and widely investigated [13]. In terms of nuclear claddings, one key requirement is reduced oxidation kinetics with high-temperature steam and hence significantly reduced heat and hydrogen generation. Two primary strategies are being developed and evaluated worldwide. One approach is developing oxidation-resistant monolithic or layered cladding materials, such as iron (Fe)-based alloys, SiC composites, MAX phase materials, and multilayer molybdenum (Mo) cladding[14-15]. These new cladding concepts represent a long-term strategy that requires significant engineering redesign to the cores. Another obvious and more near-term approach could be the modification of the surface of existing and available Zr alloy claddings, typically by protective coatings, to improve the oxidation resistance, as it does not significantly alter the existing UO_2/Zr-based alloy cladding fuel design. To protect Zr alloy surfaces against oxidation Zr alloy surfaces were modified by ion implantation and plasma electrolytic oxidation [16]. The utilization of coatings to protect structural materials, such as superalloys, refractory metals, and carbon composites, is an important issue[17-18],[19].

In this work we show that polycrystalline diamond (PCD) layer grown in a microwave plasma chemical vapor deposition apparatus is a good surface protection candidate for ZIRLO and Zircaloy *2* nuclear fuel cladding surface. Diamond withstands very high temperatures, has excellent thermal conductivity and low chemical reactivity, it does not degrade over time, and (important for the nuclear fuel cladding) being pure carbon, it has perfect neutron cross-section properties. Moreover, polycrystalline diamond layers consisting of crystalline (sp^3) and amorphous (sp^2) carbon phases could have suitable thermal expansion. Here we provide a fundamental explanation of the causes of the astonishingly high corrosion prevention of Zr alloys, which is achieved through the deposition of composite PCD layers [20]. Despite long-term exposure to a corrosive environment and specific nature of the heterogeneous PCD material (diamond and graphitic phases), the anti-corrosive effect of such protective PCD layers is very significant. [4, 21-24].

2.Methodology and sample description

2.1. Growth of polycrystalline diamond as anticorrosion coating on Zr alloy surface

The chemical vapour deposition (CVD) process of diamond growth is quite different from natural diamond formation. It produces diamond from a heated mixture of a hydrocarbon gas (typically methane) and hydrogen in a vacuum chamber at very low pressures. [25]. A layer protecting the surface of zirconium alloys used in nuclear reactors characterized by the fact that it is formed by a homogenous polycrystalline diamond layer prepared by chemical vapor deposition method and is from 300 nm to 700 nm thick.

2.2 Oxidation of autoclave processed PCD coated ZIRLO and Zircaloy 2 samples

To simulate the long-term protective capabilities of PCD layers under normal conditions in a nuclear reactor, PCD-coated and reference uncoated ZIRLO samples were subjected to a series of high-temperature autoclave water tests. In accordance with ASTM standard procedures, the samples were exposed for 6, 15, 20, 30, 40, 90, 120, 150, 170 and 195 days in hot water (360 °C) at a pressure of 16 MPa, close to the conditions found in the primary circuit of a PWR, at the Westinghouse facilities in Pittsburgh, USA. No additional chemicals were used in the autoclave water.

To simulate the protective capabilities of PCD layers against hot steam under accident conditions in a nuclear reactor, the samples (tubes or plates) were heated to the required temperature in inert argon atmosphere for the required duration (900 °C / 1 h, 1100 °C / 1 h and 1200 °C / 20 min) exposed to steam at atmospheric pressure. All steam exposures were performed isothermally. After hot steam processing, the steam/water flow was switched off after the required time, and the sample was slowly cooled down under an argon atmosphere.

2.3 Ion beam irradiation of PCD coated Zircaloy 2

In order to mimic the indwelling of PCD-coated Zircaloy 2 under constant neutron bombardment, the samples were subjected to ion beam irradiation testing, by using an 1.7 MeV tandetron accelerator at Ion Beam Facility of Texas A&M University. The Zircaloy2/diamond samples were irradiated by Fe ions of 3 MeV at room temperature, to a fluence of 1.95×10^{16} cm^2. The beam spot size was about 5mm×5mm and beam rostering was used to guarantee the irradiation uniformity. The irradiation took about 5 hours and beam heating is measured to be less than 20°C. The study is aimed to test radiation tolerance of the deposited diamond layer by using ion bombardments to simulate its behaviors under neutron environments.

2.4 Mass spectrometry for PCD coated ZIRLO and Zircaloy 2 samples

The amount of hydrogen dissolved in the ZIRLO after steam exposure (at either operating conditions or a high temperature simulating accident conditions) was determined with a G8 GALILEO analyzer. This analyzer operates on the basis of the inert gas fusion principle, which requires the fusion of the sample material in a graphite crucible at high temperatures. The concentration of the outgoing hydrogen is subsequently measured with a mass spectrometer. No correction for an oxide layer was applied; consequently, for heavily oxidized samples from thermogravimetric experiments, the measured value of the hydrogen concentration does not exactly reflect the actual concentration in the sample.

3. Results

3. 1. Oxidation of autoclave processed PCD coated ZIRLO and Zircaloy 2 samples

In order to determine surface oxidation under standard reactor conditions ZIRLO and Zircaloy2 fuel cladding and plates coated by a 300 nm, 500 nm or 700 nm PCD layer were processed in hot water at 360 °C for 6 to 185 days. After all these tests, the Zr samples were still coated by the protective PCD

layers (confirmed by Raman spectroscopy and SEM) [26-30]. Tab. 1 and Fig. 1 displays weight gains measured after hot water processing of PCD coated ZIRLO samples and uncoated reference ZIRLO samples, in all cases the PCD coated ZIRLO samples have a lower weight gain than uncoated samples. Qualitatively the same results were observed after exposure to hot steam (400 °C) for 4 days. In this case the weight gain for a 300 nm PCD layer coated Zr sample was 7.8 mg/dm^2, whereas the weight gain for an uncoated ZIRLO sample was 13.2 mg/dm^2. A key requirement is effective protection of ZIRLO surfaces against oxidation and hydration under standard operating conditions (360 °C). Oxidation of PCD-coated ZIRLO surfaces after more than 100 days in 360 °C hot water was significantly decreased (35-55%) compared with that of unprotected ZIRLO processed under the same conditions.

Table 1. Weight gains (mg/dm^2) measured after autoclave tests of uncoated ZIRLO samples (fuel cladding and plates) and samples coated with 300 or 500 nm of PCD. The samples were processed in 360 °C hot water for 6, 15, 30, 90, 120, 150, 170, and 195 days under primary circuit conditions in a PWR in accordance with ASTM standard procedures. The greater relative weight gain of the uncoated ZIRLO plates and fuel cladding indicated stronger oxidation of the unprotected surfaces [4, 24].

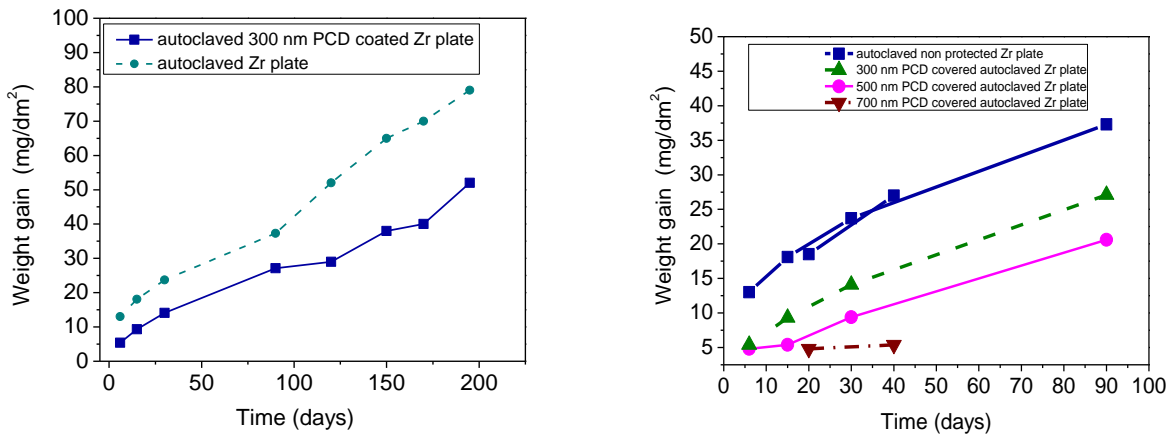| Sample type	PCD (nm)	Weight gain (mg/dm^2) of autoclaved samples							
		6 days	15 days	30 days	90 days	120 days	150 days	170 days	195 days
Tube	300	9.4	15.5	19.6	33.3	31	30	41	-
Tube	500	7.7	13.6	19.1	31.5	-	-	-	-
Plate	300	5.4	9.3	14.1	27.1	29	38	40	52
Plate	500	4.8	5.4	9.4	20.6	-	-	-	-
Tube	0	15.1	20.6	26.2	40.3	52	66	68	-
Plate	0	13.0	18.1	23.7	37.3	52	65	70	79

Fig. 1: (a) weight gains (mg/dm^{-2}) measured after 6, 15, 30, 90, 120, 150, 170 and 195 days of exposure to hot water (360 °C) for uncoated and 300 nm PCD-coated ZIRLO plate samples. (b) weight gains (mg/dm^{-2}) measured after 6, 15, 20, 30, 40 and 90 days of exposure to hot water (360 °C) for uncoated, 300 nm PCD-coated, 500 nm PCD-coated and 700 nm PCD-coated ZIRLO plate samples. Thicker PCD layers provide ZIRLO plates with stronger protection against oxidation than thinner layers [4, 24].

PCD's coating on ZIRLO was tested at extremely high temperatures of hot steam (900 – 1100 °C) for 60 minutes (simulation of accident conditions). Even at steam temperatures up to 1100°C the PCD coated Zirlo 2 samples have a lower weight gain (lower surface oxidation) than uncoated samples (Tab. 2). The CVD apparatus setting is extremely important: The best protective effect was achieved by a 500-700 nm PCD coating on ZIRLO plates, following hot water processing (360 °C, 20 - 40 days) surface oxidation was reduced by more than 50%. The apparent higher PCD protection effectivity of ZIRLO plates compared to ZIRLO tubes is caused by non-coverage on the inner surfaces of tubes compared with complete coverage of plates [26-30].

Tab.2: Weight gains (g/dm^{2}) measured by thermogravimetry of uncoated Zirlo2 (fuel cladding) samples coated with 300 nm of PCD. The samples were processed in 900, 1000 and 1100 °C hot steam for60 minutes. The greater relative weight gain of the uncoated Zirlo2plates and fuel cladding indicated stronger oxidation of the unprotected surfaces.

Temp.	Time	Weight gain	
[°C]	[min]	[g.dm^{-2}]	
		Coated	Reference
900	60	0,55 ± 0,01	0,64 ± 0,01
1000	60	2,14 ± 0,01	2,87 ± 0,01
1100	60	3,83 ± 0,01	3,98 ± 0,01

3.2.. Mass spectrometry for PCD coated ZIRLO and Zircaloy 2 samples

For the samples processed in hot water (360 °C) for 90 days, the hydrogen concentrations were measured by means of mass spectrometry. The obtained results showed that uncoated ZIRLO fuel cladding had a higher hydrogen concentration (37 ppm) compared with 500 nm PCD coated ZIRLO fuel cladding (31 ppm) and plates (21 ppm). The same analysis was conducted for uncoated and 300 nm PCD coated Zircaloy 2 fuel cladding after hot steam processing (1100 °C for 60 min and 1200 °C for 20 min). The highest hydrogen concentration was found in the uncoated samples. For hot steam processing at temperatures above 900 °C, the uptake of hydrogen into the unprotected material was very high (Tab. 3). Compared with ZIRLO samples protected with 500 nm of PCD, the hydrogen concentration in the unprotected ZIRLO samples was found to be larger by one order of magnitude. The relative standard deviation of the hydrogen concentrations was less than 6.4%. In simulated nuclear reactor conditions the penetration of H into Zr alloy are reduced due to PCD coverage, both in the case of short-term elevated emergency temperatures up to $1100^{\circ}C$ (for Zircaloy2), and in the long-term (up to 195 days-ZIRLO) maintained standard temperatures ($360-400^{\circ}C$). Therefore, PCD coverage can reduce the amount of fuel which is removed from the reactor due to cladding surface corrosion and extend fuel burning.

Table 3. Average hydrogen concentration measured after hot steam processing at 1100 and 1200 °C hot steam for 60 min and 20 min respectively of uncoated (reference) Zircaloy 2 tubes and PCD coated (500 nm) Zircaloy 2 tubes. Compared to PCD protected Zr a much larger hydrogen concentration was found in unprotected samples confirming PCD layer's protection of Zr alloy against H penetration[4].

Temp. (°C)	Time (min)	Weight gain (g.dm^{-2})		Average hydrogen concentration (ppm)	
		Coated	Reference	Coated	Reference
1100	60	2.14	2.87	51	571
1200	20	3.83	3.98	63	520

3.3. Ion beam irradiation of PCD coated Zircaloy 2

The behavior of PCD coated Zircaloy 2 in a neutron flux environment was simulated by Fe ion beam irradiation. After Fe^{2+} beam irradiation (10 displacements per atom/dpa, 3 MeV Fe^{2+}, fluency of 1.95×10^{16} cm^{-2}), and hot steam processing PCD films grown in the CVD apparatus have been shown to exhibit structural integrity. The diamond radiation damage dose dependence was shown in [26] where the effects of neutron irradiation (($1–5$).10^{20} cm^{-2} fluence range) on chemical vapor deposited diamond were investigated. Despite an increase in unit-cell volume (4.5%) the crystalline structure remain stable. In the case of neutron irradiated diamonds (4.8 and 16.3 x 10^{20} cm^{-2} fluence) the irradiated diamond density

decrease (accompanied by structural changes) was in majority cases between 12 and 25 %, with the average of 17 % .We showed that the use of PCD coating can potentially provide valuable time to deal with unplanned operations, especially during undesirable accidents in nuclear reactors, where additional time is crucial.

6. Discussion

We show that ZIRLO and Zircaloy 2 fuel cladding samples can be effectively protected against oxygen and hydrogen uptake at both accident and working temperatures in water-cooled nuclear reactor environments by coating the ZIRLO and Zircaloy 2 surface with PCD layers grown in a microwave plasma chemical vapour deposition apparatus. The CVD apparatus used for PCD preparation could be scaled up, such that it would be capable of coating full lengths of nuclear rods.

Major points concerning Zr alloys new anticorrosion strategy are [4, 21]:

- A key requirement is effective protection of ZIRLO surfaces against oxidation and hydration under standard operating conditions (360 °C). Oxidation of PCD-coated ZIRLO surfaces after more than 100 days in 360 °C hot water was significantly decreased (35-55%) compared with that of unprotected ZIRLO processed under the same conditions.

- after ion beam irradiation Zircaloy2 (10 dpa, 3 MeV Fe^{2+}) the diamond layer shows satisfactory structural integrity with both sp^3 and sp^2 carbon phases.

- Compared with ZIRLO samples protected with 500 nm of PCD, the hydrogen concentration in the unprotected ZIRLO samples was found to be larger by one order of magnitude after 1 hour at 1100 °C in autoclave, The samples processed for 90 days in hot water (360 °C) the uncoated ZIRLO fuel cladding had a higher hydrogen concentration (37 ppm) compared with 500 nm PCD coated ZIRLO fuel cladding (31 ppm) and plates (21 ppm).

Under standard operation conditions in nuclear reactors PCD layer will maintain its as-grown properties and will participate in dissipation of heat released during the reactor operation and will protect the Zr alloy from corrosion related to diffusion of the hydrogen atoms from dissociated water molecules into the Zr alloy. Additionally, in the case of any temperature or mechancal induced expansion of Zr alloy, the PCD layer will benefit from its sp^3 and sp^2 nature of hybridized carbon where flexible sp^2 carbon are able to accommodate the volume expansion of the alloy without disrupting the PCD layer integrity. PCD layers prepared by CVD technology can be also used as anticorrosion protective layer for Zircaloy 2 fuel claddings even at elevated temperatures (950°C) when α phase of Zr changes to β phase which is more opened for oxygen and hydrogen diffusion. The PCD layer blocks the hydrogen diffusion into the Zr alloy surface protecting the material from degradation.

According to we found that the role of PCD as a barrier against the penetration of oxygen and hydrogen into Zr alloy (ZIRLO, Zircaloy 2) is very complex and protects Zr alloy in hot steam/water environments in three major ways:

Firstly, the closed stable PCD layer prevents the Zr alloy from direct interaction with water molecules.

Secondly, during PCD growth and hot steam oxidation carbon atoms from the PCD layer penetrate into the underlying material creating carbides in the zirconium oxide layer, as well as at the ZrO_2/Zr interface and even in the bulk Zr alloy. In this way, carbon changes the original material structural, chemical and physical parameters so that conditions for oxygen and hydrogen penetration through the Zr alloy surface layer are exacerbated.

Thirdly, penetrating carbon changes the original ZrO_2 layer n-semi conductivity to a mixed n-and p-type, which also affects Zr oxidation effectivity. The set-up electric field can markedly affect charge carriers transport through oxide/metal interface. For unprotected Zr alloy with an n-type semi-conductive surface layer, O anions from water dissociation $(2O^{2-} + 4H^+ \rightarrow 2H_2O)$ and pass redundant electron(s) through the n-type semi-conductive ZrO_2/Zr alloy interface leading to oxygen directly oxidizing the Zr alloy Mixed n-and p-type of ZrO_2 semi conductivity changes the distribution of electric fields at the metal/semiconductor interface which further exacerbated conditions for Zr oxidation.

7. Conclusions

The protection of Zr alloys surfaces against corrosion by 300-700 nm thick polycrystalline diamond layers may be applied to a wide range of functional elements for nuclear reactors, such as fuel assembly elements. This includes, in particular, parts of commercially operated power producing light-water reactors PWR, BWR, VVER and heavy-water reactors CANDU. Important facor for protection of Zr surface against corrosion by PCD coating is carbon penetrating from PCD layer during hot steam oxidation into underlying material and worsen the whole system setting for hot steam/water corrosion. The described protective layer could potentially increase such reactors' operation safety and prolong (40% more) the Zr alloys lifetime in nuclear reactors under standard working conditions. Protective PCD layers may prolong the lifetime of nuclear cladding and consequently enhance nuclear fuel burnup. PCD layer can also serve as a passive element for nuclear safety. Costs for PCD coverage will increase the original cost by less than 1%.

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