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Pyrolytic carbon coating of Zircaloy-4 tubes at relatively low temperatures

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Abstract

A new technique has been carried out to coat the inner surface of Zircaloy-4 tubes with pyrolytic carbon at relatively low temperatures. The coating gas was a mixture of commercial butane gas as a source for carbon and argon gas as a carrier and diluent gas. Some factors affecting the coating process have been investigated. These factors were: (i) coating temperature (250–450°C), (ii) coating time (1.8–5.4 ks) and (iii) flow rate of commercial butane gas (0.83×10^{-6} and 1.5×10^{-6} m³/s) at a nearly constant flow rate of argon gas (1×10^{-6} m³/s). A photo-cell-reflection system has been used to determine the low coating weight gain. The results of this investigation indicated that the coating weight gain increased by increasing the coating temperature, time and flow rate of commercial butane gas in the studied ranges. The coating efficiency of pyrolytic carbon coatings increased by increasing the coating temperature and decreasing the flow rate of commercial butane gas. © 1997 Elsevier Science B.V.

1. Introduction

Fuel bundles of the CANDU¹-37 element type are used to fuel CANDU power reactors with burnups of 8,000–12,000 MWD/T. This burnup limitation has been attributed to the susceptibility of Zircaloy clad to fail under fission gas attack even with the existence of carbon inner coating of the clad (CANLUB). Therefore, new fuel designs which could allow for substantially higher burnups would call for improved coating of the fuel clad.

The initial coatings of CANDU claddings, were made by flooding the inside of Zircaloy tubes with Acheson colloids 'DAG-154'. Then, these tubes were dried in air and backed in vacuum at 350°C for 4 h to remove excess hydrogenous materials and leave an adherent coating of about 50% theoretical density [1,2]. Also, graphite coating was achieved in lab-experiments by dipping the tubes in a solution of colloidal graphite in water or isopropanol [3,4].

The presence of graphite on fuel cladding has demonstrated no deleterious properties in defective fuel performance. Tests have not revealed any problems from interaction of graphite with UO₂ or cladding tube [5,6]. The benefit of the graphite layer may come about in one or more of the following ways:

- (a) By acting as a lubricant and thus the stress concentration over cracks in the UO₂ pellets are reduced.
- (b) By adsorbing or absorbing fission gas products such as iodine and in-turn mitigating the SCC problem.
- (c) By forming a physical barrier between the clad and the fission products from the fuel.

In light water reactor (LWR) fuel elements no consistency in the effectiveness of carbon as PCI/SCC remedy has been demonstrated. However, a potential for substantial improvement in power ramp failure resistance has been indicated [7].

Recently, deposition of pyrolytic carbon (PyC) by the thermal cracking of hydrocarbon gases (methane, propane, butane and natural gas) has found great interest in the nuclear field [8]. Pyrolytic carbon was used as a coating for nuclear fuel particles in the advanced high temperature gas cooled reactors. Also, it was used as a coating layer surrounding the fuel kernels of the new production modu-

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¹ CANadian Deuterium Uranium. Registered trademark.

lar high temperature gas cooled reactor (MHTGR) together with silicon carbide (SiC). Such coating layers act as a vessel to retain the fission gas products [8].

In the present investigation, a new technique was carried out to coat Zircaloy-4 (Zry-4) tubes with pyrolytic carbon coating by the thermal cracking of commercial butane gas diluted by the carrier gas of argon at relatively low temperatures (250–450°C). The diluent gas controls the deposition rate and improves the diffusion conditions by increasing the mean free path of gas molecules [9]. Some factors affecting the coating process have been investigated. These factors were: (i) coating temperature (250–450°C), (ii) coating time (1.8–5.4 ks) and (iii) flow rate (FR) of commercial butane gas $(0.83\text{--}1.5) \times 10^{-6} \text{ m}^3/\text{s}$ at a nearly constant argon gas flow rate of $1 \times 10^{-6} \text{ m}^3/\text{s}$.

2. Experimental work

2.1. Materials

In the present investigation Zry-4 tubes (out side diameter = 15 mm and wall thickness = 0.5 mm) provided by the Atomic Energy of Canada Limited (AECL) were used. The chemical composition of these tubes is given elsewhere [10,11]. Commercial butane (93 vol% butane and 7 vol% propane) was used as a hydrocarbon source. Argon gas (99.99% purity) was used as the carrier gas. Pyrogallol powder was used as an oxygen scavenger while calcium chloride acted to reduce moisture content in the flowing gases. A cylindrical stainless steel reactor (1.15 m long, 60 mm inner diameter and 5 mm wall thickness) was used for thermal cracking of commercial butane gas. The furnace was connected to a temperature controller and a rotary

vacuum pump. A schematic diagram of the experimental set up is shown in Fig. 1.

2.2. Procedure

Samples of Zry-4 tubes, with a length of about 70 mm, were cleaned by distilled water, followed by acetone and were then dried by warm air. The weight of each sample and its inner surface area were determined. The sample was placed in the stainless steel reactor before starting evacuation. The system was evacuated and flushed with argon gas to minimize oxygen content. Heating started and continued until the pre-decided coating temperature was achieved. The argon and commercial butane gases were introduced into the reactor and their flow rates were adjusted according to the predecided rates. The experimental procedure included the systemic variation of the coating temperature (250–450°C), coating time (1.8–5.4 ks) and the commercial butane gas flow rate $((0.83\text{--}1.5) \times 10^{-6} \text{ m}^3/\text{s})$ at atmospheric pressure. At the end of each run, the butane gas flow rate was shut off, the electric power was disconnected and the argon gas flow rate was continued to cool the sample.

The coated samples with a measurable coating weight gain were weighed to determine the weight gain of the deposited carbon per unit area by an ordinary balance with an accuracy of $\pm 0.1 \text{ mg}$. A photo-cell reflection system was used to determine the deposited carbon low weight gain. A schematic diagram of the photo-cell reflection system is shown in Fig. 2. In that system, the coated Zry-4 tubes having different deposited carbon coating thicknesses and the bare tubes were placed between the light source and the photo-cell detector. A digital multimeter was connected with the photo-cell detector to measure the induced voltage.

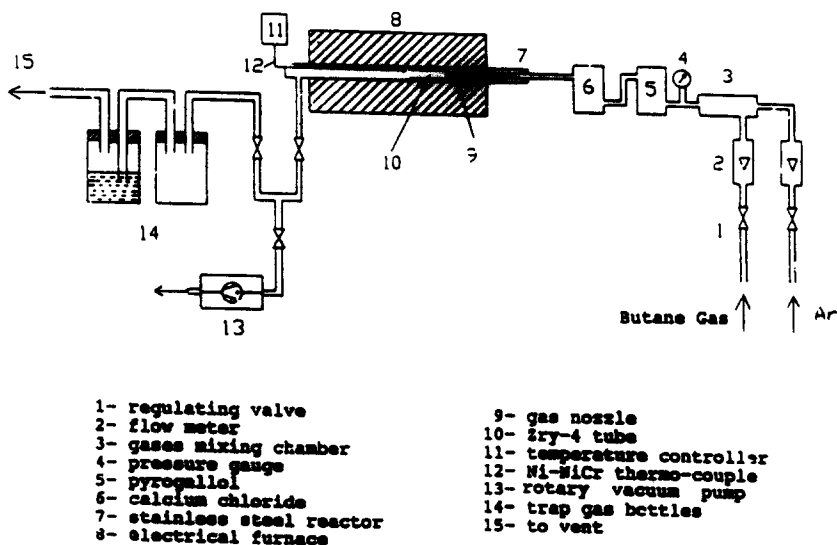


Fig. 1. A schematic diagram for the experimental pyrolytic carbon coating system of Zry-4 tubes.

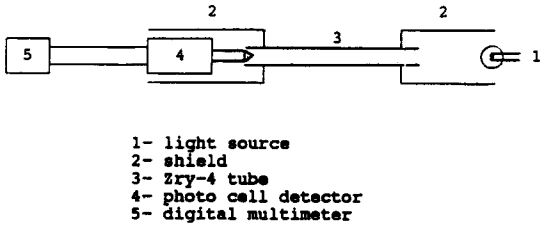


Fig. 2. A schematic diagram of the photocell-reflection system.

3. Results

3.1. Microstructure, weight gain and deposition rate

The SEM examination of the inner Zry-4 tubes surface indicated that the deposited carbon at low temperatures (250–450°C) has granular microstructure, as shown in Fig. 3. It was found that the coating weight gain is dependent upon the coating temperature, coating time and butane gas flow rate. The coating weight gain increased by increasing the coating temperature (250–450°C), coating time (1.8–5.4 ks) and the butane gas flow rate ((0.83–1.5) × 10⁻⁶ m³/s) as shown in Fig. 4.

The correlation between the logarithm of the measured voltage (by using the photo-cell system) and the coating weight gain of the deposited carbon on the inner surface of Zry-4 tubes is plotted in Fig. 5. It was possible to put that correlation in the form

$$V = V_0 e^{-\mu w} \tag{1}$$

where *V* is the induced measured voltage of the coated tube due to the reflected light, *V*₀ is a constant depending on the surface condition of the bare tube and is not sensitive to misalignments of the probe and the cladding tube (70 mm long), *μ* is the absorption coefficient of carbon and *w* is the coating weight gain.

It is clear from Fig. 5 that the correlation is a straight line with a slope of 3.6. Therefore, the correlation was put in the form

$$V = 2.225e^{-3.6w} \tag{2}$$

Eq. (2) was helpful in estimating the undetectable coating weight gain (as low as 2 mg/mm²). It was, also, possible to estimate the weight gain of the deposited carbon of the CANLUB cladding. For example the measured voltage due to placing the CANLUB cladding in the photo-cell system was 0.7 mV. Therefore, a coating weight gain of approximately 30 mg/mm² can be predicted for that cladding.

The results of the logarithm of the deposited coating rate versus the inverse of the absolute coating temperature, as shown in Fig. 6, was put in the form of the Arrhenius equation as

$$w' = Ae^{-Q/RT} \tag{3}$$

where *w*' is the deposition rate (mg/mm²/s), *A* is a constant, *R* is the gas constant = 8.3136 JK/mol, *T* is the

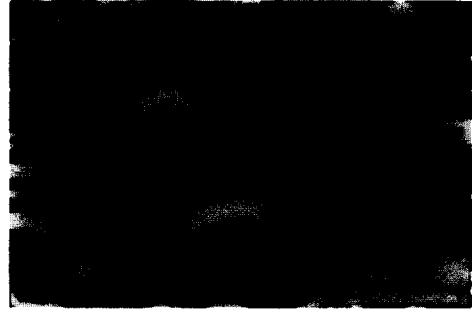


Fig. 3. SEM photomicrograph of pyrolytic carbon deposited at 450°C, coating time of 3.6 ks and flow rate of butane gas of 1.5 × 10⁻⁶ m³/s.

absolute temperature (K) and *Q* is the activation energy (J/mol) and was determined from Fig. 6 to be equal to 37.2 kJ/mol.

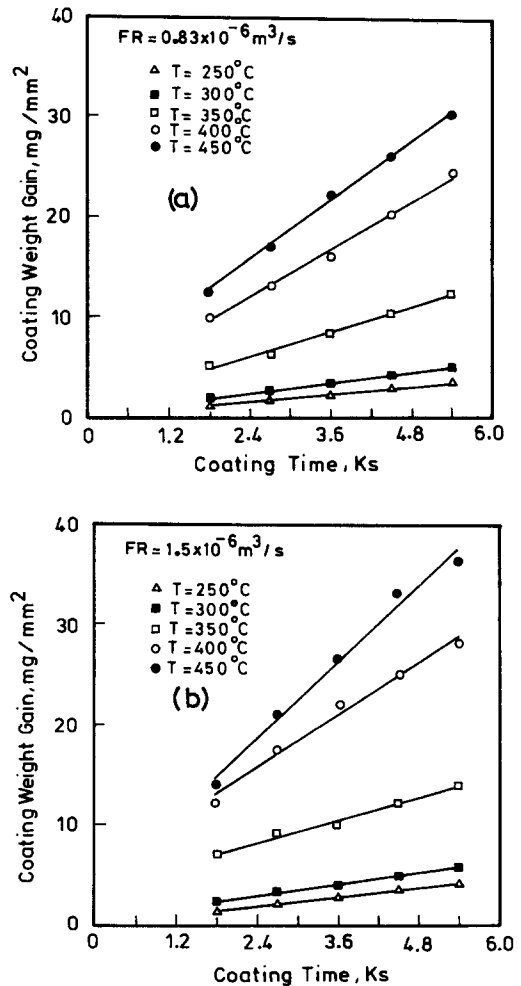


Fig. 4. Coating weight gain versus coating time at 250–450°C at flow rates of butane gas of (a) 0.83 × 10⁻⁶ and (b) 1.5 × 10⁻⁶ m³/s.

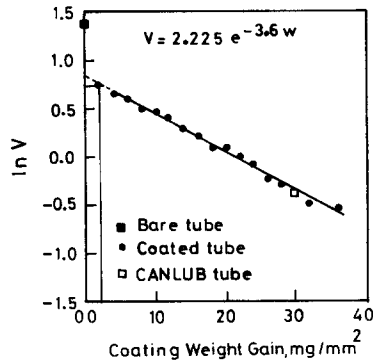


Fig. 5. The correlation between the logarithm of the measured voltage and the coating weight gain.

3.2. Coating efficiency

The coating efficiency, η , for the deposition process was determined from

$$\eta = w_d/w_i, \quad (4)$$

where w_d is the weight of carbon deposited on the total bed surface area, = deposition rate \times coating time \times total bed surface area ($\approx 0.2970 \text{ m}^2$), and w_i is the weight of carbon which enters to the system in the form of butane gas.

In the present investigation (a butane gas flow rate of $0.83 \times 10^{-6} \text{ m}^3/\text{s}$ and coating time of 3.6 ks) the volume of commercial butane gas which enters the system at room temperature is equal to 3 l. Accordingly, the weight of carbon w_i can be calculated by considering the atomic weight of carbon as 12 in the butane gas (C_4H_{10}) as

$$w_i = (3/24.45)(4 \times 12) = 5.9 \text{ g.}$$

Therefore the coating efficiency at 400°C is

$$\eta = [(0.47 \text{ mg}/\text{m}^2\text{s})(3.6 \text{ ks})(0.2970 \text{ m}^2)]/5.9 \text{ g} \\ \approx 8.5\%,$$

where the deposition rate at that temperature was $0.47 \text{ mg}/\text{m}^2\text{s}$ when the gas flow rate was $0.83 \times 10^{-6} \text{ m}^3/\text{s}$.

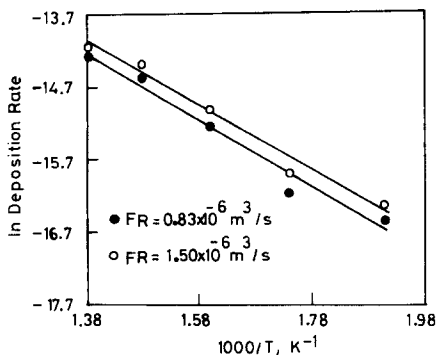


Fig. 6. Logarithm of deposition rate versus coating temperature at flow rates of butane gas of 0.83×10^{-6} and $1.5 \times 10^{-6} \text{ m}^3/\text{s}$.

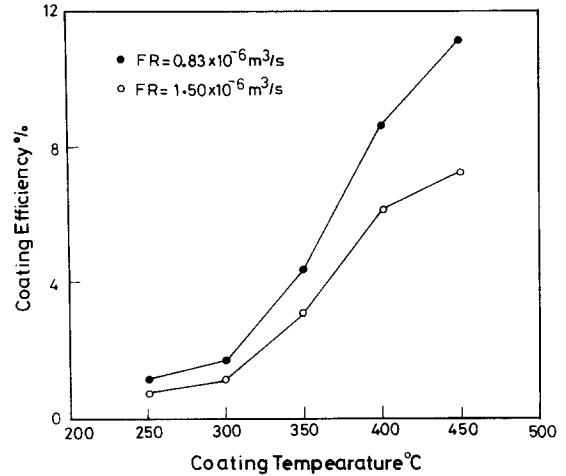


Fig. 7. Coating efficiency versus coating temperature at flow rates of butane gas of 0.83×10^{-6} and $1.5 \times 10^{-6} \text{ m}^3/\text{s}$.

The plot of the efficiency versus the coating temperature ($250\text{--}450^\circ\text{C}$) at the butane gas flow rates is given in Fig. 7. Generally, the efficiency increased by increasing temperature and by decreasing the flow rate of butane gas. For example at 250°C it was equal to 1.16 and 0.8% at the butane gas flow rates of 0.83×10^{-6} and $1.5 \times 10^{-6} \text{ m}^3/\text{s}$, respectively. However, at 450°C it decreased, from 11.11 to 7.25% as butane gas flow rates increased from 0.83×10^{-6} to $1.5 \times 10^{-6} \text{ m}^3/\text{s}$, respectively.

4. Discussion

In this investigation the thermal cracking of commercial butane gas was used to coat the inner surface of Zry-4 tubes with pyrolytic carbon. It was possible to overcome the specimens oxidation problem by using pyrogallol powder as an oxygen scavenger and minimizing moisture content in the flowing gases by using calcium chloride. Cracking of butane and propane gases takes place according to the reactions



The pyrolytic carbon deposition by the thermal cracking of commercial butane has the following advantages: (i) it takes place at low temperatures, (ii) it is an easy technique, (iii) it uses an inexpensive hydrocarbon source, simple equipment and available materials, (iv) it is carried out in a relatively short time compared to the other techniques used for the CANLUB coating and (v) it has a controllable thickness as the deposition rate in that process is very low (depending on temperature and butane gas flow rate).

However, a considerable amount of atomic hydrogen is liberated in that process. That atomic hydrogen will con-

vert into molecular hydrogen in a very short time. Hydriding of Zry-4 tubes during the coating process is expected to be insignificant as long as the cracking temperature is low ($\leq 400^\circ\text{C}$) and time is short (≤ 5.4 ks).

The use of Zry-4 as a cladding material has the advantage over Zry-2 tubes of having low Ni content (0.0004%) and in turn a high hydriding resistance. Mechanical testing (tensile and hardness tests) indicated that pyrolytic carbon coating of Zry-4 tubes resulted in insignificant changes in these tubes compared to the bare tubes annealed at the same time and temperature [11]. The tensile specimens prepared from the coated tubes showed a ductile failure mode characterized with the common dimples. These findings support the assumption that insignificant hydride was formed during the coating process which otherwise could have changed the tubes mechanical properties [12].

4.1. Microstructure of the pyrolytic carbon

The microstructure of the deposited pyrolytic carbon (as shown in Fig. 3) is granular. The microstructure of the graphite coating achieved in lab-experiments by dipping in the solution of colloidal graphite in either water or isopropanol, was also granular [3,4]. There is a lack in the available information in the open literature concerning the role of type of microstructure of the coating layer (whether formed by deposition or dipping techniques) on the SCC resistance of Zry tubes. It is worth mentioning that in SCC-tests of Zry-2 tubes coated by the dipping technique in colloidal graphite in water (coating thickness was $5\ \mu\text{m}$) the failure strain ranged between 1 and 19% [3]. Also, the cracks of that coating layer occurred at strains $< 5\%$. Therefore, it is reasonable to assume that during normal reactor operation, the cladding swelling will lead to crack formation in the coated layer. Metallographic examination of the intact irradiated fuel showed that the graphite layer often does not adhere to the cladding. Evidently perfect internal coverage of the cladding is not a requirement for improved performance [5,6].

4.2. Deposition weight gain

It has been found in this investigation that the coating temperature, time of coating and butane gas flow rate have a pronounced effect on coating weight gain. The results, as shown in Fig. 4, indicated that the coating weight gain increased by increasing the coating temperature, time and butane gas flow rate. The same type of dependence had been reported by Ogawa et al. [13] for coatings deposited from the pyrolysis of *n*-hexane at the temperature range $800\text{--}900^\circ\text{C}$.

The thickness of the deposited carbon layer was about $3\ \mu\text{m}$ as calculated from the coating weight gain of $32\ \text{mg}/\text{mm}^2$ considering a coating density of about 50% of the theoretical density of carbon [4]. It is worth mentioning that the performance of the CANDU fuel element was optimized with a graphite coating of about $3\text{--}20\ \mu\text{m}$ [1,2].

4.3. Deposition rate

It is clear from Fig. 6 that the deposition rate is very slow and it increases by increasing the coating temperature and flow rate of commercial butane gas. Je and Lee [14] reported that the deposition rate of pyrolytic carbon of propane gas increases with deposition temperature, hydrocarbon concentration and with the decrease of bed surface area. Abdelhalim [15] reported, also, that the deposition rate of pyrolytic carbon of commercial butane gas increased by increasing the coating temperature ($800\text{--}1200^\circ\text{C}$) and by increasing the hydrocarbon concentration (3–10 vol%).

Kaae [16,17] reported that the deposition rate of isotropic carbon is proportional to the number of gas-borne nuclei existing in the gas phase, the amount of carbon source available for deposition as surface carbon in the gas phase and the number of gas borne particles colliding with the substrate which depend on the conditions of the flowing gas. However, Tesner and co-workers [18] in the former Soviet Union concluded that the rate of deposition is a complex function of the reactor temperature, pressure, gas phase composition, flow rate and substrate geometry and type as well as the type of hydrocarbon precursor.

It is clear from Fig. 6 that the activation energy of the pyrolysis of commercial butane at the low coating temperature range ($250\text{--}450^\circ\text{C}$) and gas flow rate ($0.83\text{--}1.5$) $\times 10^{-6}\ \text{m}^3/\text{s}$ was $\approx 37.2\ \text{kJ}/\text{mol}$. However, Abdelhalim [15] reported a lower value for the activation energy of the pyrolysis of commercial butane of about $5\ \text{kJ}/\text{mol}$ at temperatures higher than 900°C and of about $43.5\ \text{kJ}/\text{mol}$ for temperatures below 900°C . This would indicate that mass transfer controls the deposition process at least down to 900°C , below this temperature kinetics would control the process.

4.4. Deposition efficiency

It has been found, as shown in Fig. 7, that the deposition efficiency, η , increases (from 1.16 to 11.11%) by increasing the temperature (from 250 to 450°C) at the flow rate of commercial butane of $0.83 \times 10^{-6}\ \text{m}^3/\text{s}$. However, the coating efficiency decreased (from 11.11 to 7.25%) as the butane gas flow rate was increased from 0.83×10^{-6} to $1.5 \times 10^{-6}\ \text{m}^3/\text{s}$. The same trend was noted by Abdelhalim [15] who concluded that the coating efficiency increased from 4 to 21% as the temperature was increased from 800 to 1100°C for coatings deposited on the UO_2 microspheres using a commercial butane gas (concentration of 3 vol%). Bokros [19] found no variation of the coating efficiency with bed surface area, where as Ford et al. [20] reported that the coating efficiency increased with the increase of bed surface area. Beatty [21] indicated that for propane as a hydrocarbon source the coating efficiency decreased with the increase in the hy-

drocarbon concentration at low temperatures. The decrease in coating efficiency, which means a decrease in the moles of butane and propane decomposed per mole of commercial butane gas present per hour, may be attributed to the inhibition of the decomposition of commercial butane by hydrogen [22].

5. Conclusions

The most important conclusions of this investigation can be summarized as follows.

(1) Coating of Zry-4 tubes by pyrolytic carbon through the thermal cracking of commercial butane gas at the low temperatures (250–450°C) is a practical and inexpensive technique.

(2) The coating weight gain increases by increasing the coating temperature, coating time and flow rate of the commercial butane gas.

(3) It is possible to determine very small coating weight gains by using a photo-cell-reflection system through the relationship

$$V = 2.225e^{-3.6w},$$

where V is the measured voltage and w is the coating weight gain.

(4) The average deposition rate of pyrolytic carbon coatings is very slow at the temperature range of 250–450°C.

(5) The coating efficiency decreases by increasing the butane gas flow rate at the same cracking temperature.

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