

INNER SURFACE PROTECTION OF NUCLEAR FUEL CLADDING, TOWARDS A FULL-LENGTH TREATMENT BY DLI-MOCVD, AN OPTIMIZED COATING PROCESS

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ABSTRACT

Internally protecting a full-length nuclear fuel cladding is still a challenge. Amorphous chromium carbide coatings deposited with DLI-MOCVD were previously investigated for this purpose. This paper explores several ways to optimize the DLI-MOCVD process in order to achieve a uniform thickness profile of the coating in 1 m long cladding segments. Simulated growth rate profiles are compared with experimental ones. It appears that except at low temperature and pressure, the model fits very well. It is finally possible to smoothen the profiles by decreasing the pressure and the temperature, increasing the total gaseous flow rate, applying a temperature gradient along the cladding or by considering a two-step process. While experimental works are currently focusing on the treatment of a bundle of 16 cladding segments of 1 m long, the conclusive simulation in a full-length cladding is comforting us to keep upscaling the process.

1. Introduction

Fukushima-Daiichi accident triggered a worldwide effort devoted to the enhancement of global existing safety in nuclear reactors. The first fission products containment barrier consisting of cladding tubes are one of the studied crucial improvements through the development of EATF (Enhanced Accident Tolerant Fuels). Among all EATF short-term or mid-term solutions, various concepts focus on the protection of fuel cladding on their outer wall during accidental conditions such as LOCA (Loss of Coolant Accident) [1]. For this purpose, a ionized PVD Cr deposition process is under development [2].

However, when exposed to a coolant-limitant accident, all coated Zr-based cladding concept suffer from the same weakness after their ballooning and burst. High-temperature steam have access to the unprotected inner surface of the cladding, leading to its fast inner oxidation and secondary hydriding, which induces significant additional embrittlement of the claddings. In order to assess this issue, a special gas-phase process, DLI-MOCVD (Direct Liquid Injection – MetalOrganic Chemical Vapor Deposition), was investigated in the perspective of depositing an inner-side protection coating all along fuel claddings [3,4].

The development of this deposition process is underway, keeping in mind that nowadays, a technological demonstration of a process is not enough. Economic viability and ecological impact have to be quantified in order to assess the entire industrialization potential of the process. These aspects will be discussed along this paper.

In order to efficiently protect the internal surface of a nuclear fuel cladding, the deposited coating has to satisfy 3 main criteria: (i) to be a good barrier against high-temperature oxidation, (ii) to exhibit a homogenous thickness all along the cladding (4 m) and (iii) to show a thickness of several microns. The first point was previously demonstrated for amorphous chromium carbide α -CrC_x coatings [5]. This is in agreement with the good corrosion and oxidation resistance of Cr₇C₃ at high temperature [6]. The second and the third criteria can be addressed with the help of numerical modelling. In fact, simulating the coating deposition guides us towards several potential solutions for these last two points. Indeed, we were able to demonstrate the possibility in two steps to successively and alternatively inject the reactive gas phase at each end of the cladding segment to achieve a good compromise between both thickness uniformity and average thickness of coatings grown at 673 K [7]. However, for an industrial development, the optimisation of the deposition conditions in one step is preferred to simplify the process, which is precisely the aim of this paper.

From the state of the art in the CVD community, it is known that both low deposition temperature and total pressure are mandatory in order to get a good uniformity of thickness in large scale reactors and/or complex shape pieces. However, it usually leads to a very poor conversion yield of the precursor, which significantly impacts the cost of the process when expensive metalorganic compounds are used. For the selection of the chemical system of this study this issue has been considered and it was adequately selected to allow the integration to the process of a loop-recycling system, which is very rare in CVD, thus compensating this drawback [3]. Therefore two main routes have been explored here: (i) the application of a temperature gradient in the reactor axis to compensate the precursor depletion, responsible for the decrease of the growth rate along the axis and (ii) the conjugated effect of low temperature, low pressure and high total gaseous flow rate, these last two parameters reducing the residence time of reactive species inside the reactor. This paper deals with these results and particularly focuses on deposition at temperature as low as 623 K.

2. Experimental

Bis(ethylbenzene)chromium (denoted BEBC) was supplied by Strem Chemicals Inc. It is a liquid mixture of bis(arene)chromium compounds $[(C_2H_5)_x(C_6H_{6-x})]_2Cr$, where x varies from 0 to 4 and BEBC represents about 70% of this mixture. It was used as chromium source as-received because all these compounds exhibit very similar properties as molecular precursor

for CVD. Toluene (purchased from Sigma Aldrich, purity 99.8%) was used as solvent. The liquid solution, BEBC and toluene, is injected in a vaporization chamber heated at about 423 K. N₂ was chosen as dilution gas because it is inert at the low temperatures used (≤ 723 K). After being generated in the vaporization chamber, the reactive vapor is then transported inside the Zr-based fuel cladding segment via thermostated stainless steel pipes. The fuel cladding tube (reactor) is positioned along the axis of a tubular three-zone furnace. Activated by the temperature, the reactive gas phase decomposes and forms amorphous chromium carbide coatings ($a\text{-CrC}_x$) inside the cladding. A roots pump and a monitored butterfly valve allows working at controlled reduced pressure (130-3330 Pa). Between the reactor and the vacuum pump, a liquid nitrogen cold trap condensates the reaction byproducts, as well as the unreacted chemicals.

3. Results on 1 m long fuel cladding segment

As stated in the introduction and evidenced in previous works [5], amorphous CrC_x coatings are suitable to protect fuel cladding from oxidation at high temperature. The efficiency of these protection barriers is due to their homogeneous and glassy-like morphology. Furthermore, they exhibit a dense and amorphous structure without grain boundaries. These structural features were found for all the growth conditions previously investigated, e.g. in the temperature range 673-773 K and the total pressure 660-6660 Pa [3,5,7].

A preliminary optimization of the deposition process of these coatings was recently realized through experimental parameter adjustment assisted by multi-physics computational simulations and using a simplified kinetic model in order to demonstrate its viability to protect cladding segments in a pilot reactor. Details on the model and the simulations are described elsewhere [7]. Further simulations have also been used here with CFD-ACE multi-physics simulation software package [8] to improve the optimization of the process in term of thickness uniformity. Numerical simulations provide robust kinetic and multicomponent transport models capable of predicting amorphous chromium carbide coating growth in claddings, from centimetric segments to metric ones and even to full-length cladding tubes (4 m) as it is presented further. As a result, computational simulations provide a set of optimal deposition parameters to coat homogeneously the inner surface of a fuel cladding segment of 1 m long.

The main issue we have to address first is the non-uniformity of the film thickness along the 1 m fuel cladding segment. Such issue is inherent in any CVD process when long segments have to be coated without moving them in the furnace. Generally the growth rate goes through a maximum before decreasing downstream as shown for instance in Fig. 1. This is related to the decrease of the precursor concentration along the cladding tube due to its consumption. As a result, the goal is to set accurate parameters in order to get both the best thickness uniformity of the film and an average thickness sufficient to act as a good sacrificial barrier in EATF conditions.

Several parameters can be tuned to control the growth rate of the film along the fuel cladding, the most important being: (i) the growth temperature, (ii) the total pressure and (iii) the total gas flow rate. They have all a great influence on the growth rate of the film particularly because they influence the residence time of reactive species in the tube. Obviously the working temperature is the most critical parameter in CVD because it acts both on the main features of the deposited material and on chemical reactions which are thermally activated according to an Arrhenius kinetic law.

In the present work, three ways have been investigated to improve the growth rate profile along the cladding tube, all of them coupled with numerical simulations:

- (i) Inject successively and alternatively the reactive gas phase at each end of the fuel cladding tube (two-step process);
- (ii) Applying a linear temperature gradient along the reactor (positive downstream);

- (iii) Further optimization of the growth conditions by studying the effect of previously unexplored conditions as low temperature (≤ 673 K), low pressure (≤ 660 Pa) and high total flow rate (≥ 500 sccm) in order to decrease the residence time of reactive species by increasing the vapor velocity.

3.1 Influence of the total pressure

The first films were synthesized at a temperature and a pressure of 673 K and 2000 Pa respectively and 500 sccm of N_2 as dilution gas. Fig. 1 shows the variation of the thickness of such a coating along the cladding tube. The growth rate reaches a maximum near the entrance of the tube, and then it decreases continuously downstream due to the consumption of the precursor. These conditions lead to a relatively sharp thickness gradient to such an extent that there is no deposit near the exit of the tube. There is a good agreement with the corresponding simulation curve confirming that the simplified model used is useful in these conditions. In this simulation, to gain calculation time, the thermal profile applied on the external wall of the fuel cladding segment is isothermal. Interestingly, the figure also shows that the thickness uniformity is improved by decreasing the pressure but this is detrimental to the average growth rate and it is not suitable.

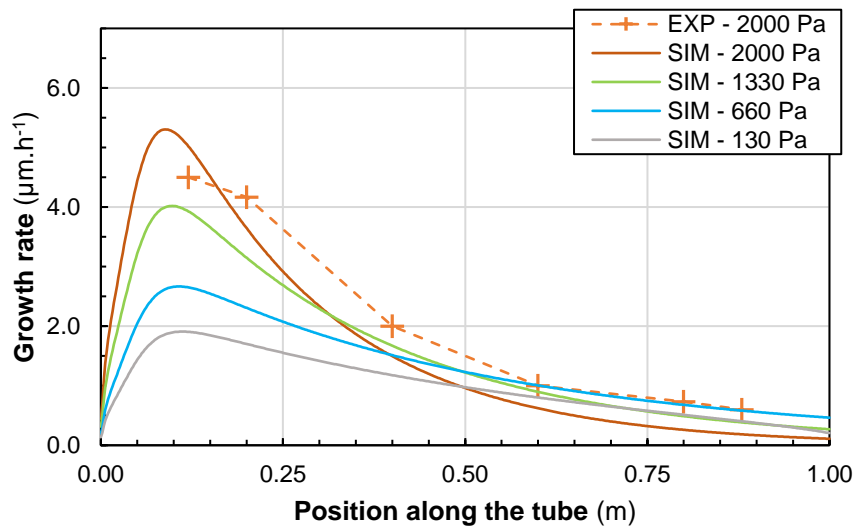


Figure 1: Influence of the total pressure on the growth rate of α -CrC_x coatings inside and along the cladding tube: experimental data obtained at 2000 Pa and 673 K is compared to simulation curves for different pressures in the range 130 to 1330 Pa while other parameters are kept constant (500 sccm of N_2 , 4.4 sccm of BEBC and 108 sccm of toluene)

3.2 Application of a temperature gradient along the tube

In order to compensate for the axial depletion of the reactive species, a typical method is to enhance thermally the growth rate of the film along the tube. As the three-zone furnace allows setting an axial temperature gradient, the second investigated solution consists in applying a positive temperature gradient. In that case, the temperature at the entrance of the furnace is set lower than that at the exit. A quasi-linear gradient is achieved by setting 648 K at the entrance of the furnace and 673 K at the exit. The pressure is reduced at 660 Pa. Fig. 2 (a) shows the experimental growth rate profile (red symbols joined by the dashed line), compared with two simulated curves. The first one (red continuous line), uses the experimental thermal profile measured inside the cladding segment, while an ideal linear thermal gradient is applied for the second one (blue continuous line). These two thermal profiles are presented in Fig. 2 (b).

Actually, our commercial three-zone furnace was not designed to provide a very good linear thermal gradient but rather an isothermal profile. However, a better knowledge of the thermal

field provided by the furnace allows the numerical modeling to calculate a more realistic growth rate profile and to fit better experimental data. It is also worth noticing that, as predicted, by simultaneously decreasing the pressure and using a temperature gradient, the growth rate profiles become a little bit more uniform, but not yet suitable. However this method remains a promising route.

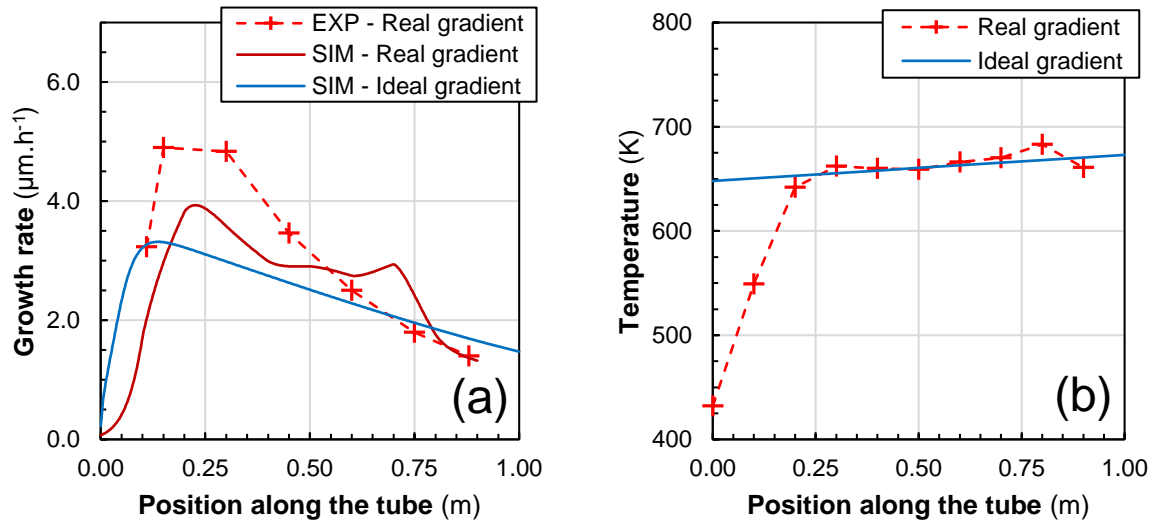


Figure 2: (a) Experimental growth rate profile of a $a\text{-CrC}_x$ coating deposited inside a 1 m long fuel cladding segment at 660 Pa, with a thermal gradient (648 to 673 K), 500 sccm of N_2 , 8.8 sccm of BEBC and 98 sccm of toluene and (b) real and ideal thermal gradient profiles

3.3 Influence of the total flow rate

Towards the objective to uniformly coat the internal surface of a 4 m long fuel cladding, the growth rates have to be mitigated, as well as the reaction yield. That is why we investigated working at even lower temperature and higher velocity of the gaseous phase. The working temperature and pressure were set at 623 K and 660 Pa respectively and the N_2 flowrate varies from 500 to 1000 sccm. Fig. 3 displays the experimental thickness profile for each experiment, compared with simulated ones where an ideal isothermal profile is applied on the outer-wall of the cladding.

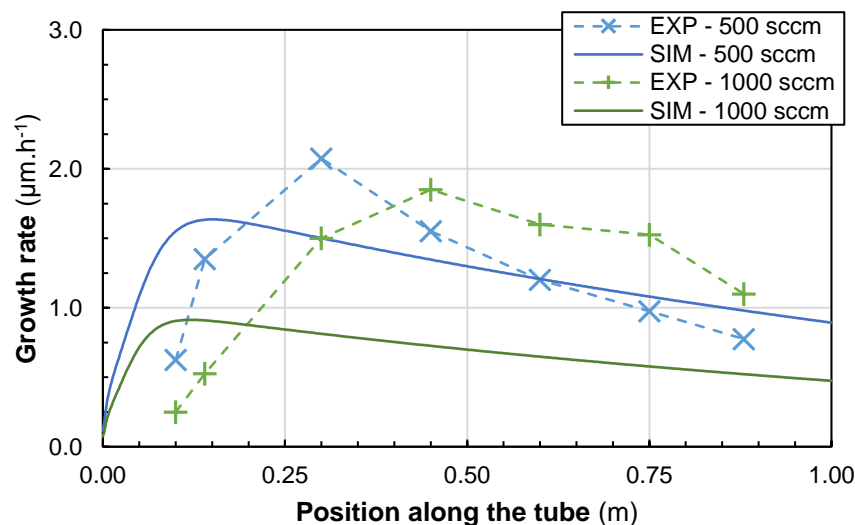


Figure 3: Experimental growth rate profiles of a $a\text{-CrC}_x$ coating deposited inside a 1 m long fuel cladding segment at 660 Pa, 623 K, 500 and 1000 sccm of N_2 , 8.8 sccm of BEBC and 98 sccm of toluene compared with simulated ones

By combining the effect of a low temperature and pressure, it is possible to obtain flatter growth rate profiles. The numerical model of the coating deposition provides correct tendencies. An increase of the dilution gas flow rate leads to an increase of the gases velocity. The residence time of reactive species is shorter, decreasing the maximum growth rate and slightly smoothing the profile. Although the simulation does not fit well experimental data the tendencies are good. The disagreement could be due to limitations in the simplified model used that did not hold in these conditions as very low temperature (623 K).

3.4 Alternative injection at each end of the cladding tube

As mentioned in the introduction, the process can be carried out in two deposition steps where the reactive gas phase is alternatively injected at each end of the cladding tube without stopping the furnace and without venting in ambient air the cladding before running the 2nd step (only a short purge under N₂ could be applied before the 2nd step). To simulate experimentally this idea and simply demonstrate its feasibility, the furnace was stopped after the 1st run, and then the cladding tube was reversed once it was at room temperature with a passage to the ambient air. As a result, the two steps correspond to the deposition runs performed in the two directions. All the parameters are kept constant during the two steps (673 K, 1330 Pa and 500 sccm) and each run has the same duration of 3 h. In such conditions, the experimental growth rate profile along the tube is displayed in Fig. 4. As expected, the thickness profile is quite symmetrical. It however exhibits two maxima, near the entrance of each run, that means near each end (around abscises of 0.20 m and 0.85 m) once the two-step process is finished.

Applying these experimental conditions, a numerical simulation was performed using an ideal isothermal profile. The simulated results are also drawn in Fig. 4. The numerical results are in very good agreement with the experimental ones although the growth rates were slightly overestimated at the beginning of the deposition in the segment. Moreover, there is a slight shift of the two maximum values of the simulated growth rate profile towards the exterior of the furnace due to the non-ideality of the real furnace temperature profile, where the working temperature is not achieved through the whole furnace but on a limited length.

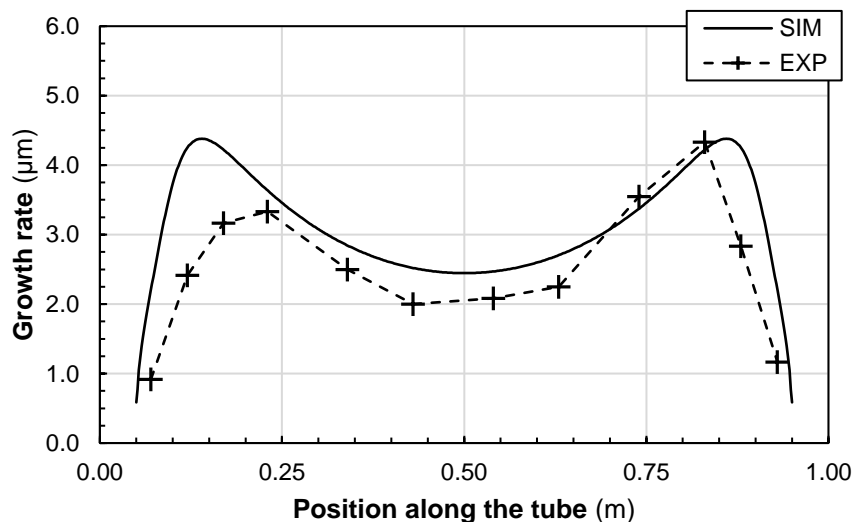


Figure 4: Experimental growth rate profile of a α -CrC_x coating deposited in two steps inside a 1 m long fuel cladding segment at 1330 Pa, 673 K, 500 sccm of N₂, 4.4 sccm of BEBC and 108 sccm of toluene compared with simulated one (flow direction of the 1st run to the right)

The “reversing method” could be an alternative to get more uniform films. The fact that the thickness profile is symmetrical is also an advantage. This method however requires performing the deposition in two steps, which does not seem to be a problem for an industrial process since the reactive gas phase can be monitored alternatively towards each end of the cladding tube.

3.5 Deposition temperature

The last investigated way to make the growth rate profile as uniform as possible is a decrease in the working temperature of the furnace. This effect is well-known theoretically and experimentally for CVD processes. Indeed, as shown in Fig. 5, the growth rate profile of a deposition at 623 K is much smoother than the one at 648 K. The BEBC precursor is in fact very sensitive to small changes in this temperature range and the relatively low value of N₂ gaseous flow is amplifying this effect. Surprisingly, in the deposition conditions of Fig. 5, the maximum experimental growth rates are very high compared to the numerical calculations superimposed on the figure.

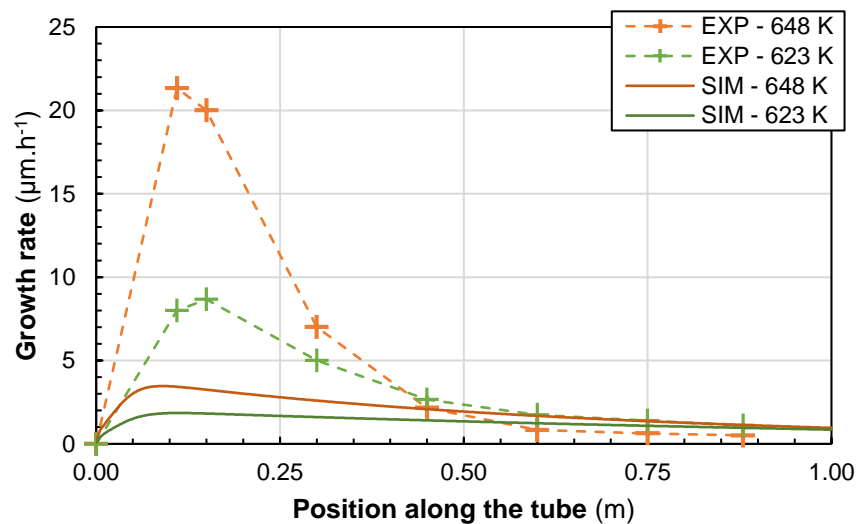


Figure 5: Experimental growth rate profiles of a α -CrC_x coating deposited inside a 1 m long fuel cladding segment at 400 Pa, 623 and 648 K, 250 sccm of N₂, 8.8 sccm of BEBC and 98 sccm of toluene compared with simulated ones

Even if the tendencies are good for our model, the fit with experimental values is clearly not satisfying for low deposition temperatures. The simplified model of α -CrC_x growth [7] ought to be revisited. It was indeed developed for similar total gaseous flow rate but for higher temperatures, between 673 and 773 K, and higher pressures, between 1330 and 130 Pa. It appears that the model would not be pertinent outside these boundaries at lower temperatures and pressures. Several reactions that were discarded at low temperature and pressure because of their minor participations to the growth mechanism could be now predominant and should be included in further works.

The coatings deposited in a cladding tube at 673 K and 623 K were characterized by scanning electron microscopy (SEM) and electron probe micro-analyzer (EPMA) directly on a piece of tube cut longitudinally. As displayed in Table 1, the chemical composition of the films is similar for all temperatures. Oxygen is present at very low levels, from 2 to 4 at.%.

Table 1: Chemical composition of $a\text{-CrC}_x$ coatings grown inside nuclear cladding tubes as a function of the deposition temperature. These EPMA data were obtained after longitudinal cut of a piece of tube expected otherwise specified.

Temperature (K)	Cr (at%)	C (at%)	O (at%)
623	66.0 ± 0.4	31.5 ± 0.5	2.5 ± 0.1
673	63.7 ± 0.9	32.6 ± 0.9	3.7 ± 0.1
723 ^a	64.5 ± 0.2	33.0 ± 0.2	2.5 ± 0.1

a) Data measured on a flat Zr-4 substrate.

Fig. 6 (a) and (b) depicts the cross-section micrographs of the films grown respectively at 623 and 673 K. For both films, the microstructure is very homogeneous and no particular morphology was evidenced. Such typical morphology suggests amorphous films with excellent conformal coverage of non-flat surfaces as confirmed by axial and radial SEM analyses. Interestingly, Fig. 6 (b) corresponds to a bi-layer coating obtained by the two-step process at the abscissa of about 0.48 m. It is as dense and homogenous as a monolithic coating. Moreover, as shown in Fig. 6 (c), the two-step deposition process at 673 K generates a thin interface between the two successive layers without affecting the overall microstructure. It is hard to be observed because it is smooth and sharp without significant change of composition. Only traces of oxygen was found by EDS line-scans in the interfacial region compare to the rest of the coating: this is due to air contamination at ambient temperature before each run. Such observation also indicates the thickness of the $a\text{-CrC}_x$ layers deposited during both steps: 5 μm attributed to the first deposition run and 7 μm attributed to the second one, which is in good agreement with the simulation. As for SEM, TEM and XRD analyses, Raman spectra of coatings grown at 623 K, either on flat Zircaloy substrates or inside cladding tubes do not show significant difference with coating deposited at higher temperature [3–5].

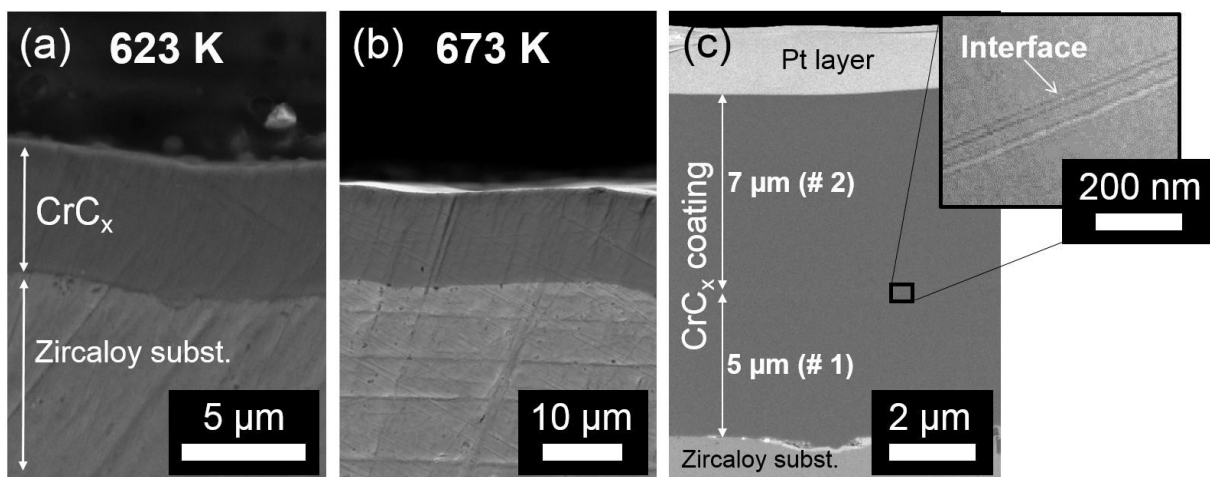


Figure 6: SEM observations of $a\text{-CrC}_x$ coatings deposited in one-step at (a) 623 K, (b) in two-steps at 673 K and (c) SEM-FEG micrograph of the coating obtained in the two-step process at 673 K with a higher magnification picture showing the interface generated between the two deposition steps

In order to get smoother (or more uniform) axial growth rate profiles, three ways were experimentally investigated. Reversing the fuel-cladding in a two-steps deposition method allows to produce symmetrical growth rate profiles. When the deposition is performed in one-pass both at low temperature (623 K) and low pressure (660 Pa), the films are relatively uniform along the 1 m fuel cladding. The ratio between the maximum and the minimum growth rates (*i.e.* growth rate measured at the axial position 0.88 m) is about 1.6 to 2.7 in these conditions. Such growth rate ratios are quite low if we compare with the experiment carried out at 673 K

and 2000 Pa where the growth rate ratio was close to 7.5. The low temperature (623 K) and low pressure (660 Pa) conditions however lead to slow growth rates (about $2 \mu\text{m}\cdot\text{h}^{-1}$) which are however still acceptable. The conversion rate of the precursor are also quite low (about 10 %), which means that a significant amount will be available to produce a coating over a greater length of fuel claddings, up to 4 m.

4. Upscaling the process

4.1 Bundle of 1 m long cladding segments

Passing from a 1 m long cladding segment to a bundle of several 1 m long segments is as important as demonstrating the full length feasibility of an inner-coated cladding. A system dedicated for coating a batch of 16 clad segments by DLI-MOCVD is described and discussed.

As for the deposition in a single clad segment where the deposition chamber is directly the cladding tube, the same principle was applied for this 16 clad segments bundle. Two major parameters have to be considered in CVD processes: the activation method of the molecular precursor and the high flow rate supply of reactive vapour. Depending on the design of the reaction chamber and the geometry that need to be coated, these parameters must be specifically adapted. They generally have to be homogeneous or gradient controlled through the entire volume of the chamber in order to ensure the uniformity of the coating thickness and properties. DLI-MOCVD process studied for the inner-protection of fuel claddings studied here is thermally activated at low temperature. Practically, the same three-zone furnace heats the clad segments which are connected to the reactive vapour supply.

A specific gas-phase distribution system was numerically designed and then validated with the help of computational fluid dynamics (Fig. 7 (a)). A homogeneous gas repartition along all the 16 clad segments can be ensured. Finally, the distribution system was fabricated through conventional machining (Fig. 7 (b)). Further developments are under consideration using additive manufacturing to achieve bigger distribution systems with more complex repartition of gas flow. The optimization of the deposition parameters in such configuration is currently in progress, based on previous results [7] and identified tendencies in this paper.

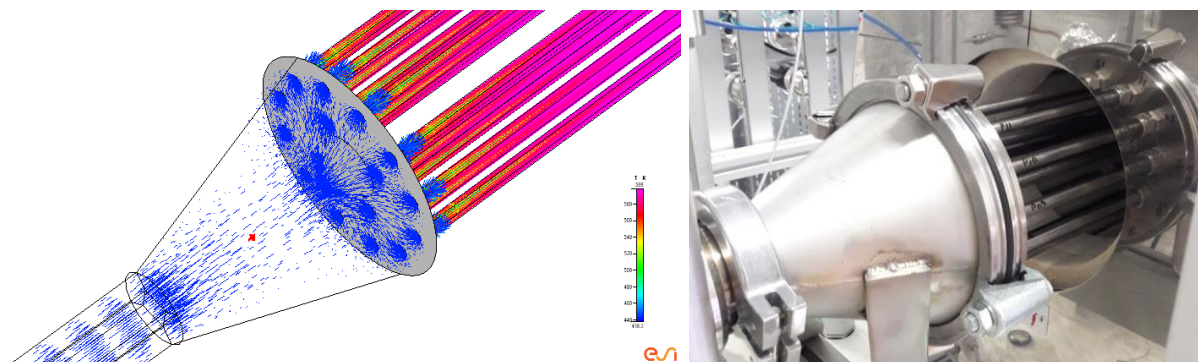


Figure 7: (a) Computational simulation of a deposition in a bundle of 16 clad segments validating the design of the gas-phase distributor and (b) conventional machining of it and installation

4.2 The 4 m long challenge

For now, only numerical modelling was conducted to have an insight of the experimental configuration required to coat a full length cladding tube. Fig. 8 shows the calculated growth rate profile of a deposition at 623 K and 130 Pa, in (a) the one-step process and (b) with the two-step process. The simulated two-step process consists in two steps of 8 h each. As the

growth rate profile in the one step process (Fig. 8 (a)) is almost linear on its decreasing part, after 0.5 m, the profile from the two-step process (Fig. 8 (b)) shows a very good uniformity of the thickness between 0.5 and 3.5 m, ranging from 12 to 15 μm . These promising calculated results are encouraging to continue the development of DLI-MOCVD process for the inner protection of nuclear fuel claddings.

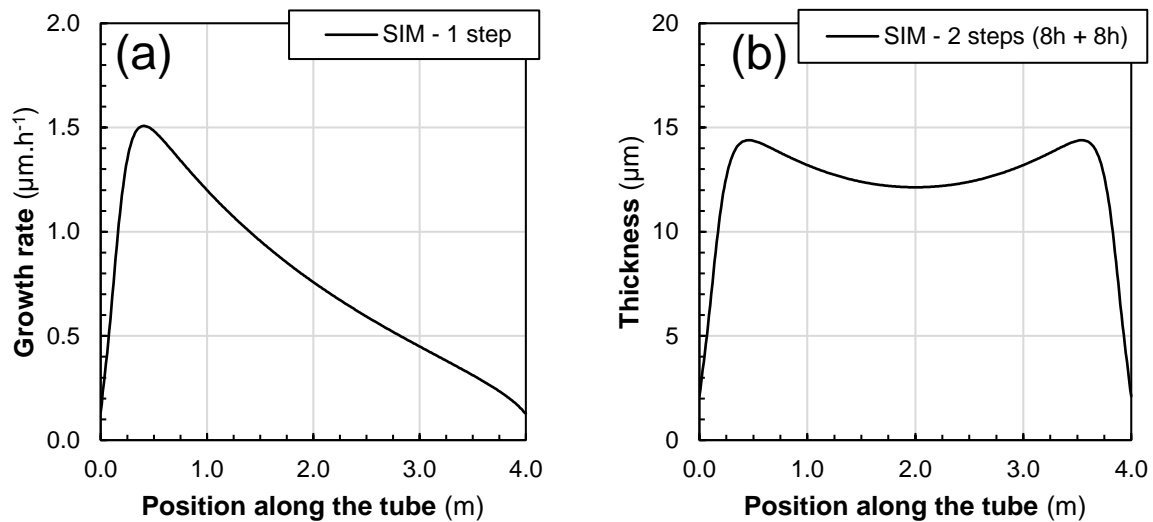


Figure 8: Calculated growth rate profile of $a\text{-CrC}_x$ deposition in a full length cladding tube (4 m) at 623 K and 130 Pa for (a) the single step process and (b) the resulting calculated thickness profile after a 8 h + 8 h two-step process

5. Conclusions and future works

The optimized set of process parameters that leads to a uniform coating deposition all along the clad segment is obtained at low temperature, low pressure and relatively high total flow rate for the chemical system used. Under these conditions, the conversion rate of the precursor is low, which strongly affects the overall efficiency of the process and is not sufficiently satisfying for an industrial point of view. However, thanks to the full recyclability of the not consumed precursor and related by-products of the family [3], this is not at this stage an issue anymore.

We suspect a disagreement with the simulation based on a simplified 4 reactions model used here which was previously proposed (1 homogeneous and 3 heterogeneous) [7]. Sensitive progress is possible towards the lowest temperatures by considering heterogeneous reactions that were first discarded to simplify the model as dissociative adsorption of the precursor. Indeed, this reaction is more and more important at low temperature and low pressure where heterogeneous reactions become preponderant instead of homogeneous pathways.

On the other hand, we keep our efforts on upscaling the DLI-MOCVD deposition process. We aim to soon demonstrate the feasibility of an internal protection of a bundle of 16 cladding segments in our current pilot. This step will be optimized and validated with the help of numerical modelling. Finally, simulated growth rate profiles on 4 m prefigures promising results and encourage us to design a bigger prototype reactor capable of protecting full-length cladding tubes.

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