Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B2-2-FrM

CVD Coatings and Technologies II

Moderators: Kazunori Koga, Kyushu University, Japan, **Francis Maury**, CNRS-CIRIMAT

9:20am **B2-2-FrM-5 Scale up of the DLI-MOCVD Process to Treat 16 Nuclear Fuel Cladding Segments in Parallel with a Protective CrC_x Coating**, *A Michau, F Addou,* CEA, Université Paris-Saclay, France*; Y Gazal, F Maury,* ***Thomas Duguet,*** CIRIMAT, France*; R Boichot, M Pons,* Université Grenoble Alpes, CNRS, France*; E Monsifrot,* Dephis, France*; F Schuster,* CEA, PTCMP, France

Direct liquid injection – metalorganic chemical vapor deposition (DLI-MOCVD) is the most advanced process dedicated to the internal protection of nuclear fuel cladding in accident conditions such as loss of coolant. A coating composed of amorphous chromium carbide CrC_x can be grown by DLI-MOCVD. It is resistant against high-temperature oxidation in air and steam. A joint development between experimental and numerical studies has led to a coating of uniform thickness inside the cladding. Optimized reactor parameters consist in a combination of low temperature (~ 600 K) and low pressure (~ 600 Pa) with a high vapor flow rate ensuring a short residence time of reactive species in the reactor.

Interestingly, CrC_x coatings deposited from the decomposition of a bis(arene)chromium(0) precursor at low temperatures, around 600 K, exhibit the same characteristics than the coatings grown at higher temperatures (623, 648, 673 and 723 K). A similar glassy-like and dense microstructure is achieved; specific to the amorphous nature of the material. No significant differences are detected in TEM, XRD, EPMA and Raman spectroscopy, regardless of the substrate (silicon wafers, 304L and zirconium alloy coupons). It indicates a strong flexibility of the DLI-MOCVD process when combined with an adequate selection of metalorganic precursor.

Since the above-mentioned materials characterizations demonstrate that low temperature coatings possess the appropriate protection properties, the low-temperature DLI-MOCVD process can be scaled-up. The final geometry to be coated is the internal surface of 4 m-long tubes with a diameter < 1 cm. Several runs are successfully achieved with a single segment, 3 segments in parallel, and finally a batch of 16 segments. 3D computational simulations of the deposition process validate the design of the gas-phase distributor flanges (for 3 and 16 segments) which are required to split homogeneously the reactive gas flow towards each segment. Experimental conditions have been extrapolated from 1 to 3 and to 16 cladding segments, resulting in the deposition of the CrC_x coating inside all segments with a uniform partition. Indeed, the total mass intakes over deposition time (g/min) are similar in all 3 or 16 segments.

Overall, this paper demonstrates the feasibility of the deposition of CrC_x coating in a bundle of several, up to 16, nuclear fuel cladding segments of 1 m in length, in order to protect them during accident conditions. This “batch demonstration” is a first step in the course of industrialization. Next step will be the deposition in a full-length cladding (4 m).

9:40am **B2-2-FrM-6 Assessment of Low Temperature CVD Routes to MAX Phases in the Cr-Si-C System***, A Michau,* CEA, Université Paris-Saclay, France*;* ***Francis Maury,*** CIRIMAT, France*; F Schuster,* CEA Cross-Cutting Program on Materials and Processes Skills, France*; T Duguet,* CIRIMAT, France*; E Monsifrot,* Dephis, France

Different CVD routes have explored for the growth of mixed carbide coatings in the system Cr-Si-C, especially the MAX phases of this ternary system. The goal was to find suitable precursors and typical growth conditions, which could be further optimized to develop an advanced process for industrial applications. For this objective, DLI-MOCVD is an emerging CVD process that combines the use of metalorganic precursors (MO) and direct liquid injection (DLI) of the reactive sources. The main advantages are a significant reduction of deposition temperatures (required for sensitive substrates and energy saving) and the production of high vapor flow rates to feed large-scale reactor.

The solid compound $Cr[CH_2Si(CH_3)_3]_4$, has been used as single-source precursor by DLI-MOCVD in a hot-wall reactor. A solution in toluene (2.9×10^{-2} mol.l^{-1}) was injected in a flash vaporization chamber directly connected to the reactor containing the substrates. The coatings were obtained under low pressure (6.7 kPa) in the temperature range 613-733 K. They are XRD amorphous and exhibit a smooth surface morphology with a dense and homogenous microstructure. Growth rates in the range 0.5-1 µm/h were obtained but the films were partially oxidized due to the high sensitivity of this single-source precursor to oxygen. The Si:Cr atomic ratio of coatings is about 1.1 which significantly lower than the amount bring by the precursor (4). This atomic ratio is relatively close to the value 0.6 of a previously reported ternary phase ($Cr_5Si_3C_2$) but far from the MAX phases Cr_2SiC (0.5) and Cr_3SiC_2 (0.33). Finally this route did not allow to control the Si:Cr atomic ratio in a sufficiently wide range, especially that of MAX phases.

To gain flexibility in the DLI-MOCVD process, a simple one-pot dual-source process has been investigated in a similar reactor. In this 2nd route, bis(ethylbenzene)chromium(0), $Cr(C_6H_5C_2H_5)_2$, and diphenylsilane, $(C_6H_5)_2SiH_2$, were used as liquid molecular precursor of Cr and Si, respectively. A solution containing both precursors in toluene with various mole ratios was used to produce the reactive gas phase via a single pulsed injector. Depositions were carried out under low pressure (6.7 kPa) in the temperature range 723-773 K on various substrates. $Cr_xSi_yC_z$ coatings have been obtained with growth rates as high as 5 µm.h^{-1} and compositions depending mainly on the composition of the injected solution. The coatings were characterized by many techniques (SEM, XRD, TEM, EPMA…) and preliminary properties including thermal stability and oxidation resistance have been investigated. It is demonstrated that DLI-MOCVD process is a promising route to deposit MAX phases.

10:00am **B2-2-FrM-7 Towards CVD of Hard Coatings Using Hetero-Metallic Precursors***,* ***Sebastian Öhman,*** *M Ek,* Uppsala University, Angstrom Laboratory, Sweden*; R Brenning,* Sandvik Coromant R&D, Sweden*; M Boman,* Uppsala University, Angstrom Laboratory, Sweden

CVD of hard coatings used for machining and cutting is a field in fast development. However, progress in this area is impeded by the lack of adequate control for nucleation and film growth, which governs the desired mechanical and physical properties of these films. In addition, today's wear resistant coatings are commonly based on single phased binary material systems, yet the increasing demands put on tomorrow’s coatings will require the development of new, multicomponent and multifunctional coatings. Such coatings can be made by combining conventional CVD with the development of new hetero-metallic precursors. This opens for new chemical pathways, better stoichiometric control, higher yields, more versatility and simplified CVD processing.

In this session, a presentation will be made regarding the use of hetero-metallic precursors for CVD. Audience will also be introduced to a newly developed 3-zone hot-wall reactor that enables the flexible deposition from such precursors, in particular those based on titanium and aluminium alkoxides. With the current experimental set-up, it is possible to use several hetero-metallic precursors at once or sequentially (i.e. pulsed CVD).

The synthesised CVD films were characterised using several methods, including XRD, SEM/EDS, TEM, Raman and RBS.

10:20am **B2-2-FrM-8 CVD of Tungsten, Tungsten Nitride and Tungsten Carbide Multilayers***, J Hulkko, K Böör,* Uppsala University, Angstrom Laboratory, Sweden*; R Qiu,* Chalmers University of Technology, Sweden*; E Lindahl,* Sandvik Coromant R&D, Sweden*;* ***Mats Boman,*** Uppsala University, Angstrom Laboratory, Sweden

Tungsten-based CVD has been investigated since the early 1960. Today, tungsten-based coatings can be found in many technological areas, ranging from electrical contacts and diffusion barriers to wear- and corrosion resistant films as well as absorber coatings in solar cells.

The aim in this study was to create new multi-layered coatings of W/WN, W/WC and WN/WC by varying the thickness and phase composition of the layers.

W/WC/WN thin films were deposited from a reaction gas mixture containing WF_6 and H_2 using Ar as carrier gas. NH_3 and C_2H_4 were added during the nitride- and carbide formation steps. The films were deposited on n-type Si(111)- and Al_2O_3(0001)-substrates, in a newly constructed CVD-equipment built in-house. This equipment is characterised by excellent repeatability using a custom software controller and a wide parameter space to work within, for instance partial pressures and temperature.

The coatings were characterised using several XRD techniques. SEM images provide microstructural information and thickness. Additionally XPS and TEM were used to gain more in-depth chemical and structural information. Vickers nano-indentation was used for hardness investigation.

10:40am **B2-2-FrM-9 Deposition of Carbon Nanoparticles Using Multi-Hollow Discharge Plasma CVD for Synthesis of Carbon Nanoparticle Composite Films***, **Kazunori Koga**, S Hwang,* Kyushu University, Japan*; T Nakatani,* Okayama University of Science, Japan*; J Oh,* Osaka City University, Japan*; K Kamataki, N Itagaki, M Shiratani,* Kyushu University, Japan

Carbon Coating films are receiving much attention as an alternative to improve the physical and chemical characteristics of material surfaces. Meanwhile, as the application field diversifies, there have been increasing requests for an improvement in optoelectronic, physical, and chemical properties of the films. Nanoparticle composite films are very promising, since they are expected to improve the film performance [1]. To further understand the films, nanoparticle synthesis and their deposition are important. In this study, gas flow and bias voltage effects on their deposition were studied, using a multi-hollow discharge plasma CVD (MHDPCVD) method. The experiment was carried out in room temperature with CH_4+Ar MHDPCVD, which can continuously produce nanoparticles [2]. Carbon nanoparticles were synthesized at 8 hollows of 5 mm in diameter where Ar and CH_4 pass through. They were transported to the substrate set 50 mm away from the multi-hollow electrode and then deposited. During the process, 60 MHz rf power of 40 W was applied and working pressure and gas ratio of Ar and CH4 were kept at 2 Torr and 6:1 respectively. Also, carbon nanoparticles that were deposited under the control of total gas flow rate from 10 sccm to 200 sccm were analyzed through a transmission electron microscope (TEM). The average size gradually decreased from about 250 nm at 10 sccm to 31.7nm at 120 sccm and the area density increased, but nanoparticles were not detected at conditions over 125 sccm . When the substrate was biased at +50V DC, the nanoparticles of 24 nm in average size were deposited at 125 sccm, becase negatively charged nanoparticles were attracted to the positively biased substrate. Hence, the gas flow rate and the bias voltage are the keys to control of nanoparticles for carbon nanoparticle composite films.

[1] Peter Greil, Advanced engineering materials / volume 17, issue 2, 2014.

[2] K. Koga, et al., Thin Solid Films 506 (2006) 656.

11:00am **B2-2-FrM-10 Hot Filament CVD Diamond Coating Technology for Cutting Tool Applications***, **Michael Woda**, W Puetz, M Frank, C Schiffers, W Koelker, O Lemmer, T Leyendecker,* CemeCon AG, Germany

Besides a variety of DLC based coatings for tribological applications, pure diamond (100% sp3 bonded, crystalline carbon) is a very useful coating material system in the group of carbon based coatings for cutting of hard to machine materials. Nowadays Diamond coatings are typically applied to cutting tools with complex geometries by means of Hot Filament CVD thin film deposition. The technology is well established on an industrial scale. The basic principle of this Hot filament CVD diamond deposition technology and the details on the corresponding coating equipment are presented here. Results of case studies dealing with cutting applications on machining of various examples of highly abrasive materials with pure CVD Diamond thin films are discussed in this work. These case studies include applications with Carbon Fiber Reinforced Plastics (CFRP) systems for aerospace industry, ceramic materials as zirconium oxides for dental applications up to direct milling of sintered cemented carbide.

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