Chemical Vapor Deposition of Tungsten Coatings on X-ray Rotating Light Anodes Made of Carbon-Based Materials

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Abstract

We developped the direct coating of a 1-mm-thick tungsten-rhenium (W-Re) layer on graphite and C/C composite (CFC) by CVD with halide precursors. Conventional process does not allow for operating temperatures higher than 1200 °C. We propose a new multi-layers interface (SiC and Re) acting as a carbon diffusion barrier, improving the maximum operating temperature. With such coatings, we are producing X-ray rotating anodes (50 mm to 150 mm diameters) and we plan to produce 250 mm diameter anodes by the end of 2013.

To obtain crack-free W-Re layers exhibiting high adhesion strength with carbon or CFC materials, even under high temperature exposure, growth process mastering is mandatory. Nevertheless its efficiency is limited by the base material thermomechanical properties. We show examples of cracks and layer delamination occuring on standard CFC grades and how to tune the CFC properties to reduce the thermal expansion mismatch.

We also developed a new method to mount the graphite or carbon composite part directly on the X-ray tube rotor stem, allowing its installation on standard X-ray tubes.

Keywords

X-ray anode, X-ray target, tungsten rhenium alloy, C/C composite, CFC, graphite, CVD, medical, computed tomography

Introduction

For X-ray medical application (such as computed tomography "CT scanner", mamography, angiography), there is a continuous tendency towards higher power X-ray beams, allowing better accuracy for medical diagnostic. The standard design for X-ray target (rotating anode) is consisting of a 1-millimeter-thick tungsten/rhenium alloy layer on a disk made of a molybdenum based alloy (Titanium-Zirconium-Molybdenum alloys, TZM). The molybdenum disk allows efficient heat storage. Nevertheless, to maximise heat dissipation, the backside of the target is often brazed to a heat conductive carboneous material (fine grain graphite).

During operation at high rotating frequency and under high power e-beam excitation, the resulting high temperature below the e-beam focal spot, as well as the mechanical loads, has led to the use of another anode design. Furthermore higher rotational frequency leads to high mechanical stress on the stator part of the housing and produces noise, so lighter materials than tungsten/molybdenum alloys are desired.

Basically, such "light" anode is made of a graphite substrate rotating at high speed (which allows for heat dissipation) on which is directly deposited a 1-mm-thick layer of refractory metal (tungsten-rich W-Re alloys), which emits X-rays under e-beam excitation. The course towards higher power for X-ray beams has led to a continuous increase of both excitation power and rotating speed. As even the better fine grain isostatic graphite shows failure under very high rotating speed and excitation power, the best candidate exhibiting higher thermomechanical properties is carbon/carbon (C/C or CFC) composite.

We developed the direct coating of a thick W-Re layer by mean of CVD with halide precursors, with the use of a multilayer interface (SiC and Re) acting as a carbon diffusion barrier and as an adaptive layer for strain relaxation.

Both thicknesses and post-growth thermal treatments have an influence on the layer adhesion strength with the graphite or CFC template. For the obtention of crack-free, adhesive tungsten layer, even under high temperature exposure, growth process mastering is mandatory but is also limited by the base material which should have compatible thermomechanical properties. As a matter of fact, a thermal dilatation similar to the one of tungsten is preferable but the base material must also show thermo-mechanical properties and a thermal conductivity at least better than the one of fine grain isostatic graphite. We have also developed a brazing method to mount the graphite or carbon composite part of the anode onto the rotor stem. It allows to install our anodes directly on standard X-ray tubes ("plug-and-play" anodes).

Overview

Acerde currently holds four CVD reactors dedicated to SiC and W-Re coatings, as well as supplementary production tools such as high temperature vacuum furnace and fine grinding machine. Its equipment allows a capacity of production of 1500 X-ray targets per year, but is also adapted to small series and prototype realizations.

Not only the CVD W-Re deposition step is performed but the whole anode production process (from raw graphite substrate to anodes ready for tube mounting) is accomplished. Acerde has thus the capability to produce fully ready rotating anodes for X-ray tubes.

The usual process flow is presented Fig. 1: from customer's anode design, a graphite body is realized, then several inspection controls are performed as well as thermal (outgassing at 2000 °C under controled atmosphere) and chemical cleanings (isopropyl alcohol solution in ultrasonic bath). The CVD deposition is then performed in one or several steps, depending if SiC is deposited or not. The W-Re track layer is finally grinded (Ra rugosity of 0,8 µm), and a mass balancing is done (unbalance less than 1 g.cm). Finally, the anode is cleaned and outgassed at high temperature (1000-1350 °C under secondary vacuum), before to be ready for delivery (after final inspection).
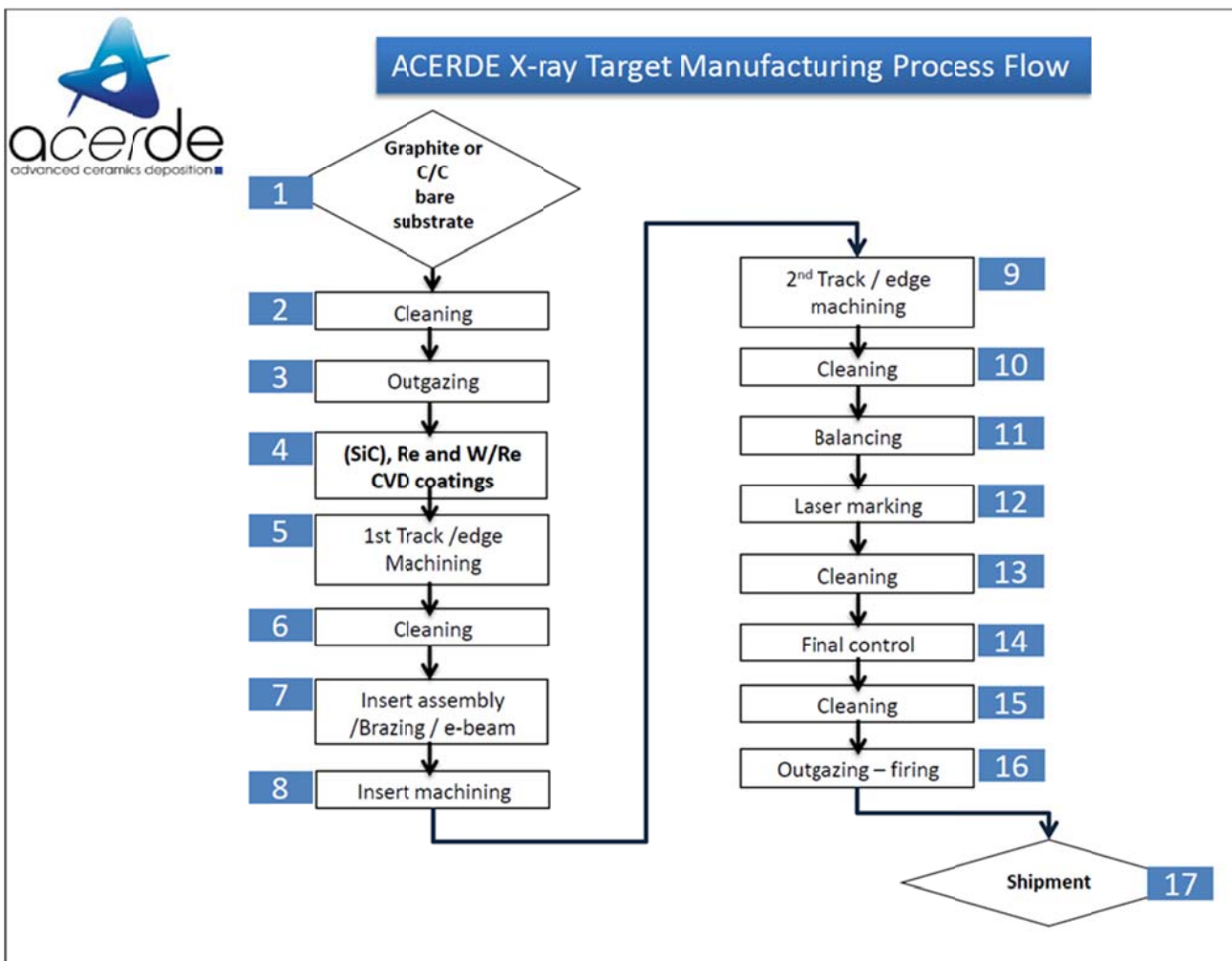
Figure 1 : Flow sheet for X-ray "light " anodes production (including the Mo insert for mounting in standard CT tubes).

Experimental

W-Re layers have been deposited by CVD on graphite or C/C composite substrates, using WF_6 and ReF_6 as halide precursors for W and Re, respectively. The deposition temperatures were in the 800-1100 °C range, at low pressure. The graphite target is heated by induction, and is rotated to ensure thickness uniformity (Fig. 2 and 3). Growth rates are in the 100-300 µm per hour range.

Typically, W-Re alloys used for X-ray emission have Re contents around 5-10 %. Such amount of Re increases the refractory metal ductility as well as improves the anode lifetime. As a matter of fact, under high temperature exposure (above 1500 °C for pure tungsten), recrystallization occurs which causes grains size increasing, surface roughening and, consequently, lower X-ray output.

The stoichiometry of the alloys is determined by precursors gaz fluxes, substrate temperature and total pressure inside the reactor. Re contents have been accessed by Castaing microprobe (EPMA) analysis on test samples (Fig. 4).
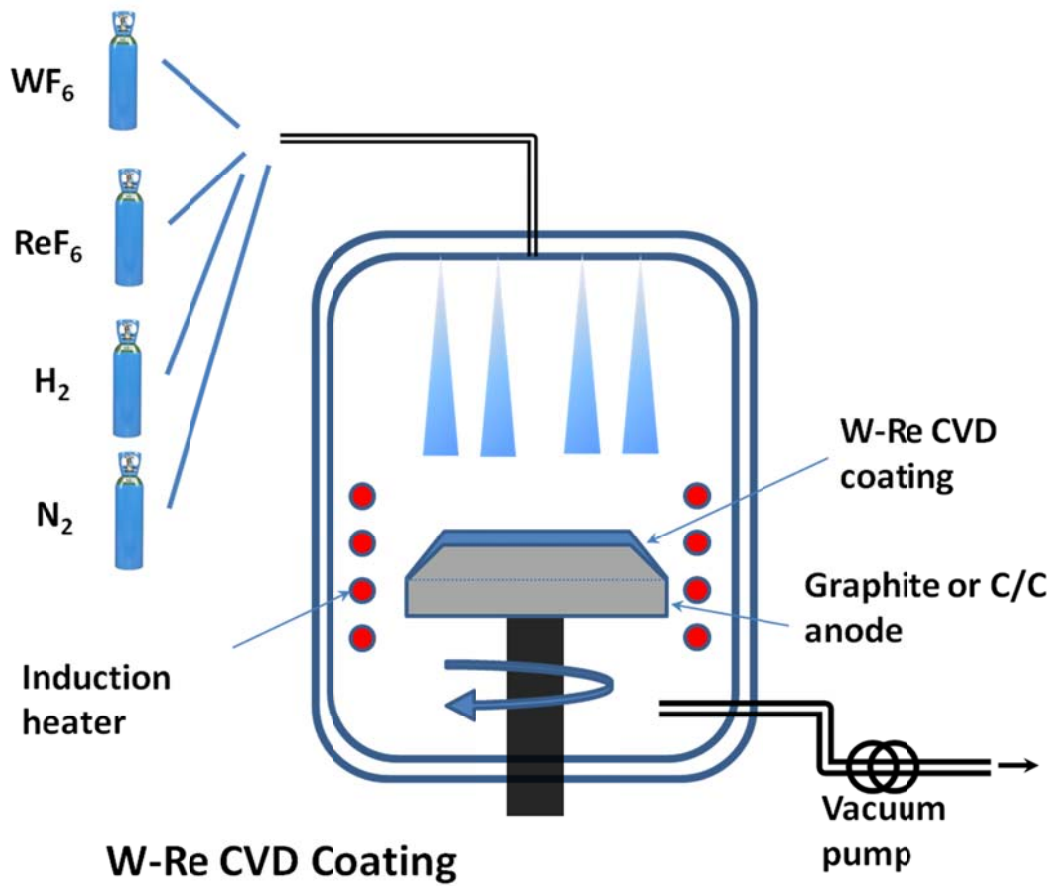
Figure 2: Schematic of the CVD reactor used for W-Re depositions on graphite or C/C targets.
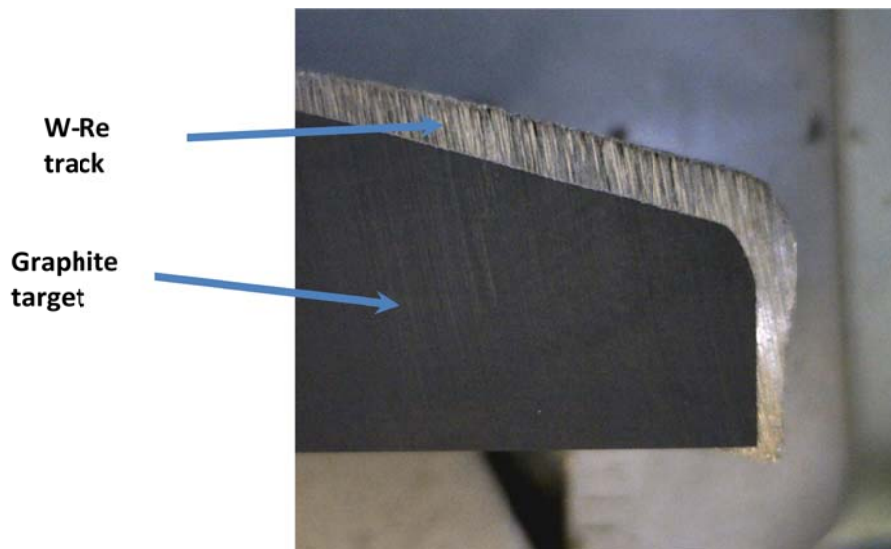

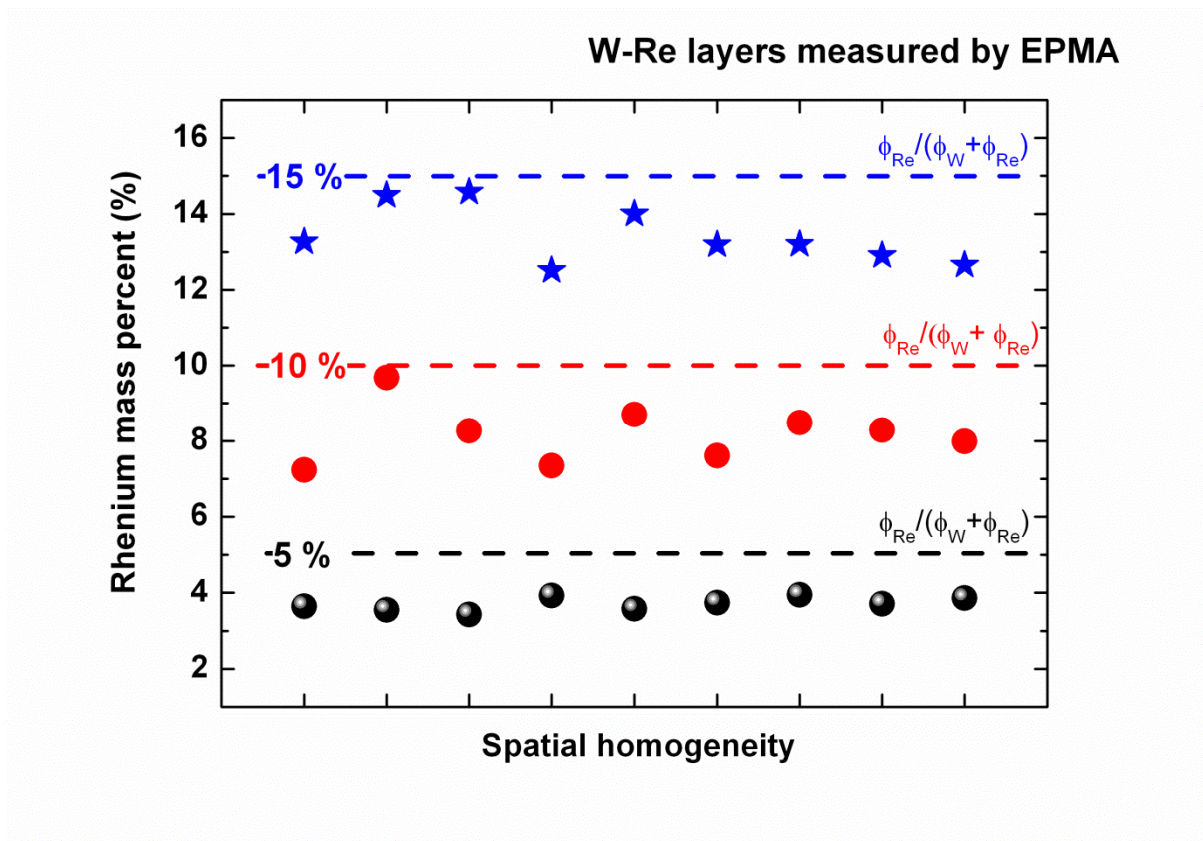Figure 3: Side view of as-deposited graphite target with W-Re CVD coating.

Figure 4: Rhenium content measured by EPMA for W-Re thick layers deposited on graphite by CVD.
Dotted lines indicate the nominal Re content calculated from precursors fluxes ratio.

By an adequate choice of the graphite or C/C composite substrate properties, we are able to deposit thick tungsten-rhenium alloys layers (e = 0,5 to 2 mm) on X-ray target body with various design and sizes (Fig. 5). CVD allows the deposition of W-Re alloys with well-defined stoichiometry. The deposited thicknesses (by varying deposition time and/or deposition rate) may easily be adjusted from 1-micron-thick layer, up to several millimeters thick coatings. Nevertheless, the deposition of thick layer is limited by the low deposition yield at high deposition rate (R > 100 μm.h^{-1}), and the high cost of precursor gases. The CVD W-Re coatings have a high volumetric density (similar to the one of bulk material) and consequently the thermal conductivity is also high, compared to less dense W-Re coatings obtained by physical vapor deposition (PVD) process, such as vacuum plasma spray, or powder metallurgy (cf. Table I).

Figure 5: Acerde CVD "light" X-ray anode with various design and size (diameters from 64 mm to 140 mm)

Table I : Physical properties of W, Re, SiC and W-Re alloys, fine grain isostatic graphite (typically used as bare substrate for CVD light targets), and TZM alloy (used for massive targets).

Property / Material	Unit	W (bulk)	W (PVD)	W-Re (6%) (CVD)	W-Re (10 %) (PM)	Re	SiC-3C	Graphite	TZM (PM)
Density	g.cm^{-3}	19,2	16-18	**19,4**	**19**	21	3,2	1,7-1,9	10,1
Coefficient of linear thermal expansion (α, CTE), 20-1200 °C	µm.m^{-1}.K^{-1}	4,5	4,7	**5,3***	**5,1**	6,2-6,9	5,6	4,5-5,9	6
Thermal conductivity @ 25 °C	W.m^{-1}.K^{-1}	173	155	**170**	**77**	48	120-360	80-130	123
Calorific capacity @ 25 °C	J.g^{-1}.K^{-1}	0,13	0,13	**0,13**	**0,13**	/	0,7	0,75	0,2
Young's modulus @ 25 °C	GPa	410	270-290	**410**	**375**	463	440	13-15	265

PVD : Physical Vapor Deposition (e.g. VPS) ; PM : Powder metallurgy

* for CVD W

W-Re Coating on Graphite Substrate

During use, the anode base material undergoes thermomechanical loads : high rotational frequency (up to 250 Hz), high operating temperature (bulk temperature in the 1100-1300 °C range, local temperature below the focal area up to 1600 °C). As a consequence, the anode body must exhibit high mechanical properties (Young's modulus, ultimate tensile strain and so on), and also high thermal conductivity, high calorific capacity as well as low chemical reactivity with W and Re materials.
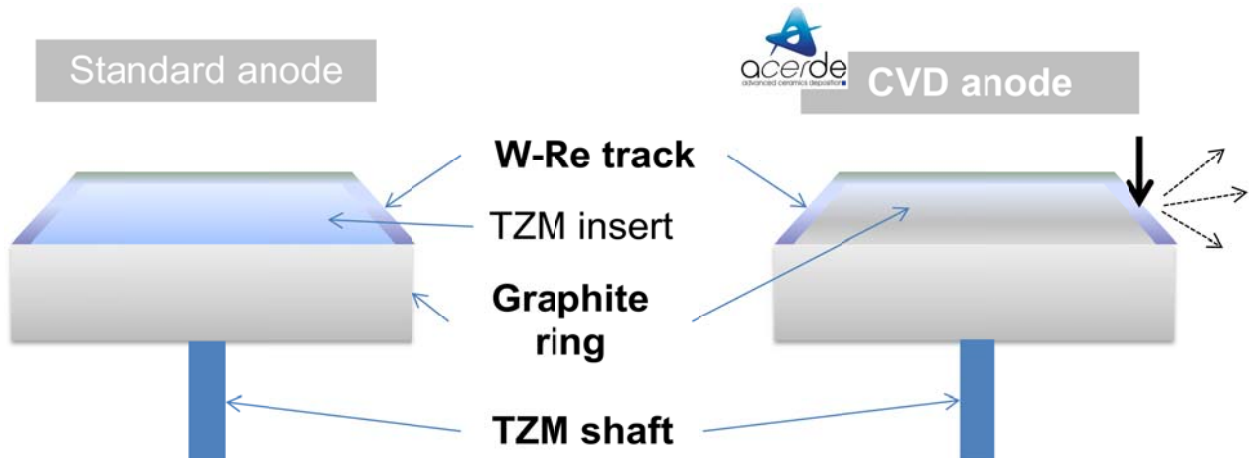

Figure 6: Schematics (side view) of standard X-ray target and light CVD anode. On CVD anode is also represented the focal spot point of e-beam excitation (black arrow) and the resulting X-ray emission (dotted line arrows).

We propose the use of a lighter material for X-ray anode usually made of pure molybdenum or TZM alloy (Fig. 6). An anode fully made of graphite offers a weight saving of more than 50 %, which significantly decreases mechanical loads on rotor bearing (TZM shaft). Furthermore, graphite allows an efficient heat transfert, which is mandatory for high operating temperatures due to the use of high power densities for the electron beam applied on the anode track.

Due to the direct deposition of the tungsten-rhenium layer on the graphite substrate, the carbon diffusion (especially at high temperature) has to be taken into account. As a matter of fact, W carburization to tungsten mono-carbide WC and tungsten sub- or di-carbide W_2C compounds at temperature above 1000 °C is a well known phenomenom [1]. On the other hand, Re does not form rhenium carbide compound in usual temperature and pressure conditions.

As a consequence, a thin (1-10 micron thick) rhenium interlayer is used as a carbon diffusion layer between the graphite substrate and the W-Re layer (hundreds of microns thick). Nevertheless, for very high temperature exposure (e.g. 1600 °C) or long time exposure at high temperature, the tungsten carbide formation is observed. Due to its lower thermal conductivity than W or Re as well as its differences in thermal dilatation and cell volume (Table II), above a thickness of a few tens of microns, W carbides layers (WC and W_2C) cause an increase of the interface temperature and a W-Re track peeling-off [2].

Table II : Physical properties of W, Re, and tungsten carbides (WC and W_2C).

Property / Material	Unit	W (bulk)	Re	WC	W_2C
Density	$g.cm^{-3}$	19,2	21	15,6	17,3
Coefficient of linear thermal expansion (α, CTE), 20-1200 °C	$\mu m.m^{-1}.K^{-1}$	4,5	6,2-6,9	5,2	/
Thermal conductivity @ 25 °C	$W.m^{-1}.K^{-1}$	173	48	29	29,3

W_2C is not thermodynamically stable below 1250 °C, and the tungsten sub-carbide layer thickness tends to continuously increases during the anode lifetime (high temperature exposure), and causes aging and failure of the X-ray target.

In a certain extend, it is possible to limit the tungsten carbide layer formation by performing post-deposition hight temperature annealing step. The metallic tungsten carbide formation is mainly controlled by C diffusion from the graphite to the tungsten layer, through the already formed tungsten carbides layers. The C diffusion is smaller in WC [3] than in W_2C, and an annealing step at temperature below 1250 °C should favor the formation of the thermodynamically stable WC layer, inhibiting the continuous growth of a W_2C layer [4] during anode operation at high temperature, under e-beam excitation. Nevertheless, such treatment does not allow a fine control of the tungsten carbide thickness evolution with time and temperature.

If using tens of microns thick Re layer, which is a costly solution, even if carbide formation is suppressed, the low thermal conductivity of the interface remains problematic.

We propose to replace the usual Re barrier layer by a multilayered interface (W/Re or W-Re/Re). It allows a control of the tungsten carburization, which remains spatially limited (*cf.* Fig. 7). This approach, combined with optimized post-deposition annealing, should improve the anode lifetime by limiting the formation of W carbides.
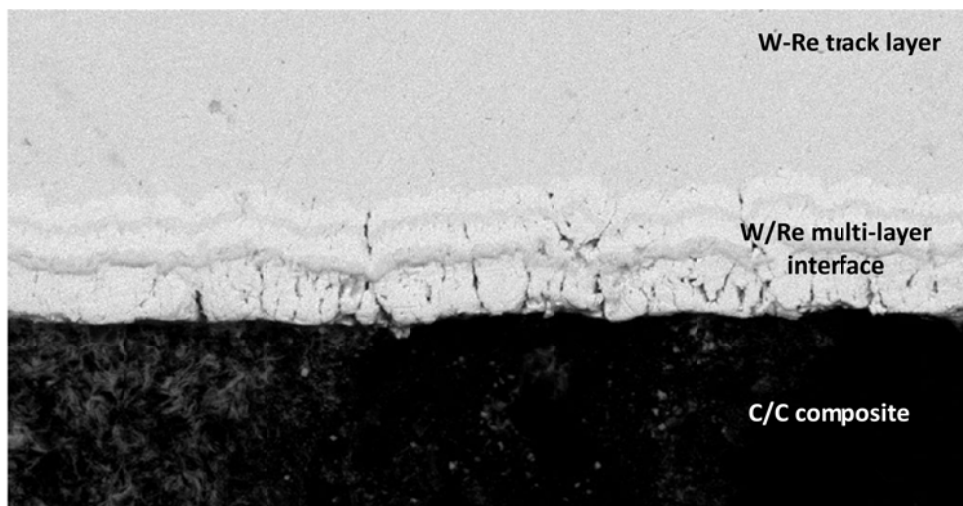

Figure 7: Side view (SEM, chemical contrast mode) of the interface between the anode body and the W-Re track, including a W/Re multilayer interface.

Additionally, we have proposed the use of an additional layer of SiC, deposited by CVD using as precursor methyltrichlorosilane (MTCS) diluted in H_2. Silicon carbide compound is also thermodynamically stable with carbon, and has a coefficient of thermal expansion very close to the tungsten one (Table I). It is also a good thermal conductor (high thermal conductivity). Moreover, SiC is widely used as an impervious coating, preventing contamination and gaz impurities diffusion from the graphite target. Nevertheless, a strong W/Re/Si/C interdiffusion has been observed (Fig. 8), with the formation of rhenium silicides and tungsten carbides compounds, even at relatively low temperature (1100-1200 °C).
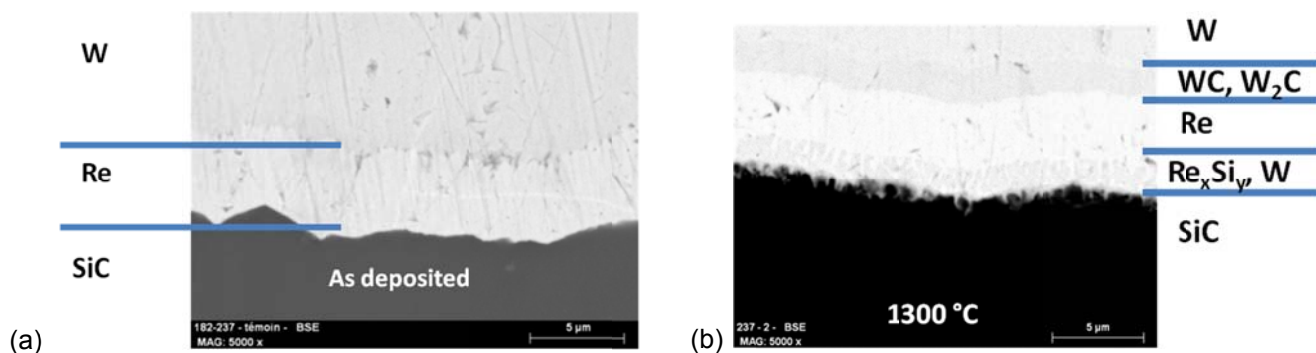

Figure 8: SEM images (side view) of a W track deposited by CVD with Re and SiC interlayers (a) as-deposited and (b) after thermal heat treatment at 1300 °C.

W-Re Coating on C/C Composite

Graphite offers an alternative material for present-day anode designs and medical applications. Nevertheless, future requirements (very high rotating speed, up to 350 Hz, high power density, and longer exposure times) will require an up-scaling of the anode design [5]. For such novel specifications, graphite as a base material for large diameters anode (Φ = 150 to 250 mm, or 6" to 10") does not exhibit high enough thermo-mechanical properties, which has led to turn ourselves to carbon fiber /carbon matrix composite as X-ray target base material.

We have experienced tungsten coatings by mean of CVD using two C/C composite grades. These two grades, among the multitude of tested C/C grades from major stakeholders, are representative of grades with properties mainly governed by the carbon fibers ("C/C 2D" grade) or by the carbon matrix ("C/C iso" grade).

The grade "**C/C 2D**" is a cloth with a 2D weaving and the grade **"C/C iso"**, showing quasi-isotropic properties, consists of long carbon fibers randomly oriented (Table III).
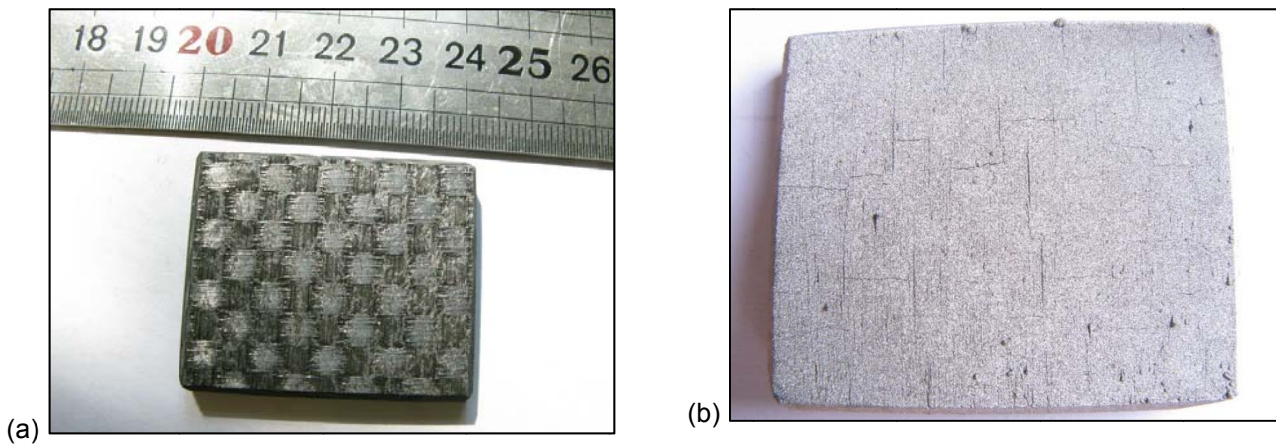
Figure 9: (a) "C/C 2D" composite grade (bare substrate) (b) CVD W layer on "C/C 2D" grade, showing a cracking network.
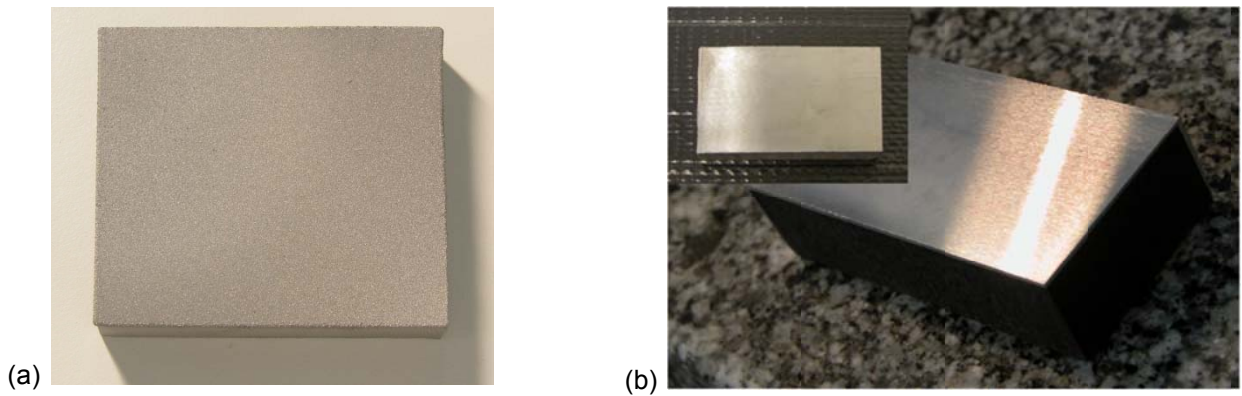

Figure 10: (a) As-deposited W CVD layer on "C/C iso" grade and (b) after thermal annealing and fine grinding .

Table III : Material properties of fine grains isostatic graphite, and C/C composite grades ("C/C 2D" and "C/C iso").

Property / Material	Unit		Isostatic graphite	C/C "2D"	C/C "iso"
Density	g.cm^{-3}		1,85	1,6	1,8
Coefficient of linear thermal expansion (α, CTE), 20-1200 °C	µm.m^{-1}.K^{-1}	$\perp$	5,9	> 7	3
		//		< 1	2
Thermal conductivity @ 25 °C	W.m^{-1}.K^{-1}	$\perp$	100	10	200
		//		40	250
Young's modulus	GPa		13	80	15
Ultimate tensile stress	MPa	//	40	170	30

$\perp$ perpendicular to the fibers weaving plane, // along the fibers weaving plane

After CVD deposition and cooling-down, the density of cracks has been used as a simple criterion to evaluate the quality of the coating.

If no crack is present (or if the crack density is very low, typically less that 1 crack.cm^{-2}), the test samples have been annealed, cut, and grinded, in order to produce additional thermal and mechanical stresses.

For W layers deposited on "C/C 2D" grade, we have clearly identified that cracking, due to post-deposition temperature ramp-down, is very dependent of carbon fiber orientation (Fig. 9). As a matter of fact, the thermal dilatation is smaller along the fiber direction than normally to the fiber axis. Thus, we observe a cracking network with preferential cracking direction normally to the fiber axis. Similar results have been obtained on various C/C 2D composite grades, from various suppliers.

For "C/C iso" grade, no cracking network is observed even after thermal treatment and polishing (Fig. 10). It has to be noticed that C/C composite "C/C iso" has very similar mechanical properties to a high quality fine grain isostatic graphite.

As a conclusion, W (and low Re content W-Re alloys) without cracking and/or peeling-off are obtained when using C/C composite showing quasi isotropic surface (fibers randomly oriented or weaving along a high number of directions). An additional criterion to perform W-Re CVD coatings without post-deposition crack formation is a CTE as close as possible of W (cf. Table I).

Brazing of Carboneous Materials for "Plug-and-Play" Anodes

The "massive" X-ray anodes (tungsten track, TZM and graphite body) are usually mounted on the TZM rotor shaft by using Ti-/Zr- braze. The brazing temperature is in the 1550-1750 °C range. For CVD "light" anodes such brazing temperature will led to W carbides formation, which has to be avoided to ensure the mechanical strength of the target/track layer interface.

We have developed a brazing process at much more lower temperatures, compatible with the CVD process. Typically, it consists in a ring-shaped Mo insert brazed on graphite using Palladium-Cobalt (Pd-Co) melted at 1200-1250 °C. This temperature allows performing the brazing step after the CVD coating steps.

Using PdCo alloys is a well-known solution for Mo/Mo brazing and ensures the mounting of the graphite anode on the TZM rotor shaft. Strengthening between the PdCo alloy and the graphite body is ensured mechanically. The Pd-Co brazing could also be done with an additional graphite coating of Ta, TaC, W or Re (in particular a W layer could allow the formation of W-C-Co alloys). We also used successfully the Pd-Co brazing for C/C targets.

Conclusion

These results allow the production of rotating light anodes with large diameters (Ø = 200 mm, up to 250 mm) comprising a carboneous body made of a carbon-carbon composite and a W-Re CVD track layer. Such rotating anodes with larger diameters, allowing larger thermomechanical loads than conventional designs, are on the roadmap for future CT scanners of various manufacturer of X-ray scanners.

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