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Coating of particles

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HTR TECHNICAL REPORT
DRAFT

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SUMMARY

HTR field was studied in the years 70-80 at Grenoble, but the programs, notably with General Atomics, were abandoned. Within Work Package 4 (Fuel Fabrication) HTR-F Shared Cost Action (Fuel Technology), it is question to retrieve the knowledge acquired in the past and to update characterisation according to the progress realised since. This study concerns coating technology of nuclear « fuel » particles used in high temperature reactors.

After the starting up of a furnace in Grenoble, the objective was to optimise coating particles. Although the principle of deposit process by CVD in fluidised bed and the choice of different precursors necessary to obtain pyrocarbone or silicone carbide are well known, the need to optimise the different layers parameters required the implementation of characterisation methods. As regards the coating density, two laboratory methods were used such as the floatation in a liquid or still the measure of the volume made by geometrical laser measurements.

Keywords
High temperature reactor (HTR), pyrocarbone (PyC), silicone carbide (SiC), chemical vapour deposition (CVD), fluidised-bed coating, nuclear « fuel ».

CONTENT

1. INTRODUCTION

Within the framework of the calls for tender of the 5-th Common Program in Research and Development for the nuclear fission, the European consortium decided to hand the technologies level developed before in the field of the fuel HTR (High Temperature Reactor). This decision was taken with the aim to improve reliability and performances of the materials. It is a question, within the European framework, to develop the coating techniques for nuclear fuel particles. The deposit, also called envelope, is realised by the technique of deposit in vapour phase or CVD (Chemical Vapour Deposition) in fluidised bed. The envelope of nuclear fuel particles represents an essential stage for the field HTR.

2. GENERALITIES

As regards the process, two CVD furnaces are available in Grenoble. The recent bibliographical review [1] [2] shows not a great evolution on the technique of deposit as well as on the various deposited layers compared with the old experience; the reference being the envelope of fissile UO_2 kernel. One distinguishes, according to the nature of the kernel, two types of envelope:

- the type BISO which contains a layer of porous pyrocarbone (or buffer) as reservoir plug to fission gases and a layer of dense pyrocarbone insuring a gases seclusion,
- the type TRISO which presents an improvement of the precedent by addition of a silicon carbide (SiC) layer as a barrier to the solid fission products, followed by a layer of dense PyC to assure at the particle a mechanical resistance.

It is to note that a particular effort is observed in the literature to optimise the retention of the envelope [3]. TRISO envelope is generally reserved for the fissile materials.

3. COATING TECHNIQUE

The application of the various coatings is realised in a fluidised bed furnace by a process of deposit in vapour phase (see figure 1). The fluidisation of balls or kernels is insured by argon flow, at the base of the furnace generally conical [4]*. The success of the operation is based, mostly, on the injection mode. For a given volume, considering the particles density, the gas flow must be sufficient to put in movement the warmed particles. Different hydrocarbons, according to the type of deposit are introduced, warmed in the contact of particles to form, near 1400 °C, an isotropic pyrocarbone (PyC) with:

- a weak density by decomposition of acetylene (C_2H_2) gas,
- higher density by decomposition of propylene (C_3H_6) or still a mixture of the two gases.

SiC coating, with a density close to the theoretical density, is made near 1600 °C by decomposition of Methyl-Trichloro-Silane (CH_3-$SiCl_3$) by barboting in hydrogenate gas.

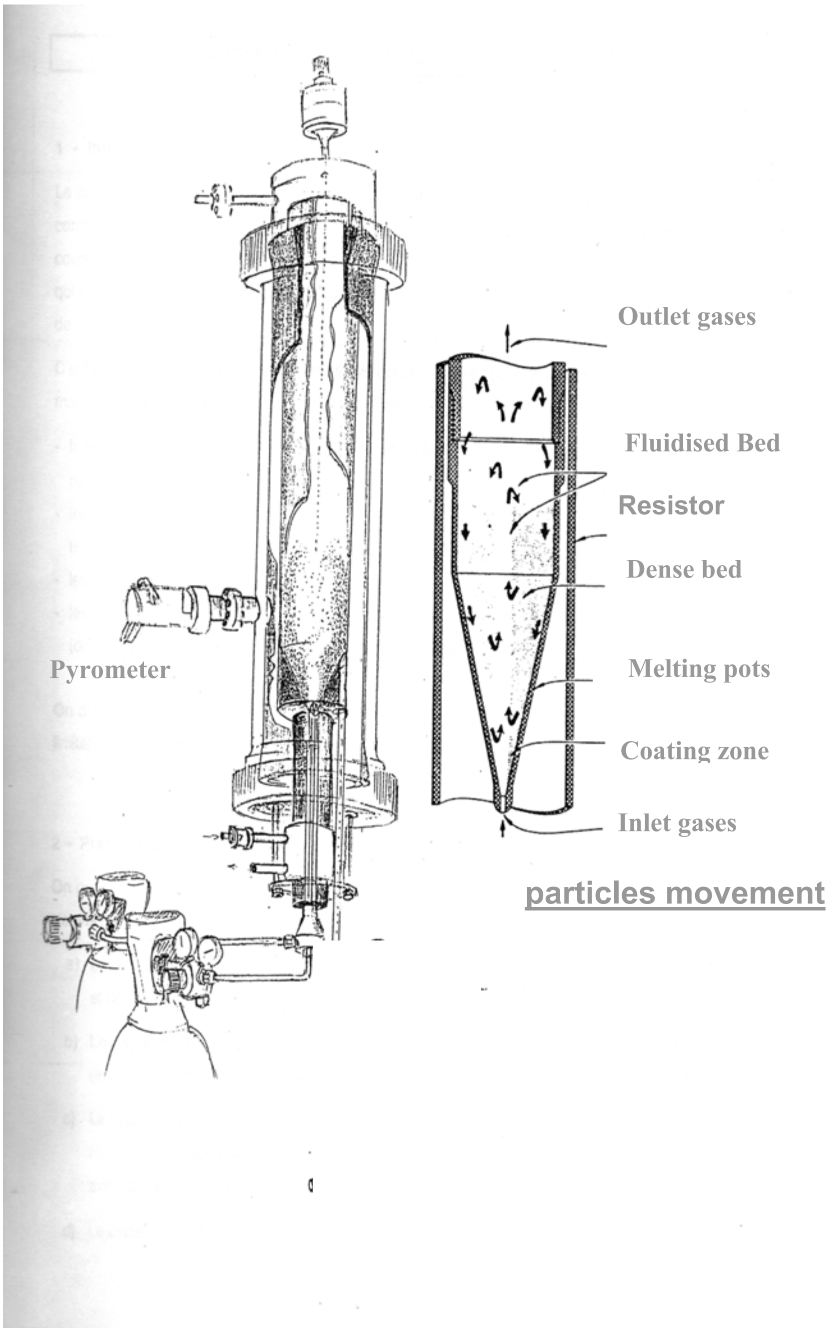

Figure 1. Schematic principal of CVD fluidised bed furnace.

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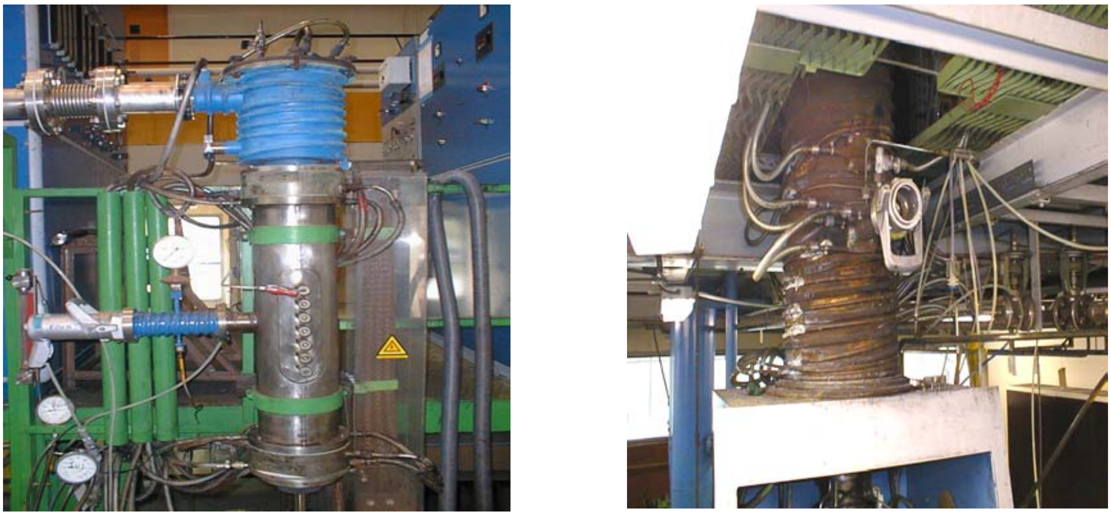
*Tests were also realised in flat furnace with injection of gases through a porous patch or still by means of multi-injectors

4. INSTALLATIONS

BISOtropic and TRISOtropic particles was made in 3 and 5 inches furnaces at CEA GRENOBLE (figure 2).

The 3 inches furnace, of English technology, was implanted at the beginning of the 70’s and allowed to study the first particles made for the reactor DRAGON.

The 5 inches furnace, settled in 1976-1977 was conceived as industrial prototype. From General Atomic, it allowed to realise various types of coated particles BISO with dense kernel, TRISO with dense and light kernel for tests under irradiation.



3 inches furnace

5 inches furnace

Figure 2. CVD fluidised bed furnaces.

4.1 Upgrade of equipments

In the aim to realise and to optimise both PyC coatings which represent ¾ of the envelope, the modifications made at first has concerned:

- the installation of C_2H_2 and C_3H_6 gases for the pyrocarbone deposit and the link with the 3" furnace,
- the modification of 3" CVD furnace (injection gases, molybdenum injector, melting pots and extension graphite piece). A modification at the top of the furnace was also studied to take off particles during the process.

The temperature is followed by a pyrometer on the external part of the melting pot. On the other hand, considering the scale of the pyrometer (1000-2000°C), it is not possible to follow the temperature during the ascent. It is planned to install a thermocouple connected with a second regulator to pilot the complete cycle.

5. QUALITY CONTROL METHOD

5.1 Laser light Scattering measurements

Laser diffraction has been used for measuring the size of the particles and also the thickness of the different layers. The apparatus, Mastersizer S, is maid by Malvern Instruments, an English company (figure 3). The laser light scattering is constituted by a laser source, followed by a collimator, measurement cells, a focal and a logarithmic detector. It is possible to analyse from 0.05 µm to 3500 µm. The technique ensures rapid analysis, less than 30 seconds for about 5000 particles, allowing rapid feedback. The particles are put into a calibrate cone and cut the source laser by gravity. Each particle, enlightened by the laser, behave itself as punctual sources of light. According to the figures of diffraction emitted by the particles, the signal treatment gives the spectrum, by edge, of the cumulated diameters, then the medium diameter of the sample.

So, it is possible to calculate, by difference, the thickness of a layer before and after the deposit thanks a taking off during the process. It is a reproducible and non destructive technique.

Figure 3. Laser light Scattering device.

5.2 Density measurements

Two methods can be used:

- WLS (Weigh Laser Scattering) method, which associated to laser scattering allows, for pyrocarbone deposit, to give a value of the material density. It consists in measuring, counting, weighing and burning a known number of particles. After burning, and then weighing again, the loss of weigh calculated allows to define the mass of deposit, for a particle. Knowing its diameter before and after deposit, the deposited volume and the density of the material can be thus calculated. As every measure (counting, weighing, size measurement) is soiled by a uncertainty to definer, a second method has been put in place.

- FCF (Floatation Coating Fragments) method used for determination of dense pyrocarbone or SiC coatings. The density of the micro fragments is measured by floatation in a liquid or a liquids mixture which we adjust the temperature (see figure 4). The principle concerns a solid, with a known density, in immersion in the same liquid and linked at a scales (precision = 0.0001 g). We can determine precisely, in these conditions and in a same time, the liquid density and so the micro fragments which are in equilibrium. This instant is chosen during the rise in liquid temperature and is defined with a great precision in maintaining a constant temperature (thermostat circulation) during the weighing of the reference solid. When the sample is in floatation in front of the solid, its density is equal at the liquid density:

$$\rho_{liq} = d_{sol} [1 + (P_1 + P_2 / P_3 + P_4)]$$

With d_{sol} = solid (alumina) density

P_1 = weight of hanging system + wire in immersion

P_2 = weight of hanging system + wire in immersion + solid in immersion

P_3 = weight of hanging system + wire + solid in air

P_4 = weight of hanging system in air

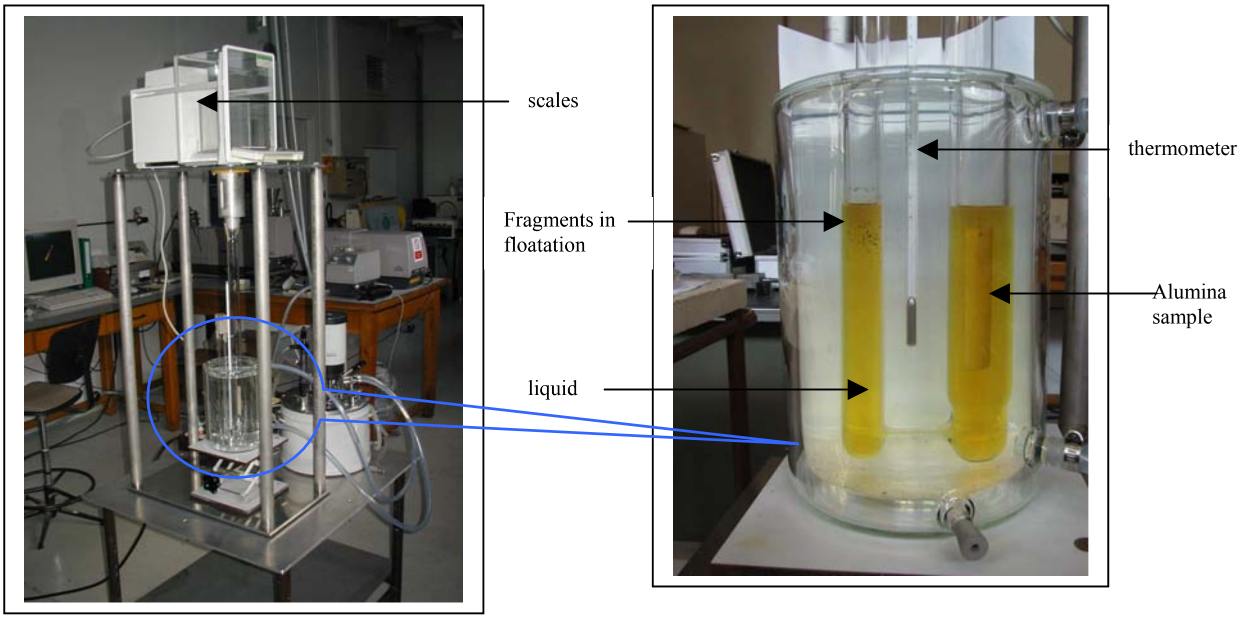


Figure 4. Floatation Coating Fragments device.

6. KERNEL CHOICE

The CVD process in fluidised bed is very sensitive to the density and objects diameter to fluidise.

Considering the specifications given (deliverable 18), the supply in simulant kernel was necessary. The best one is HfO_2 considering his density close to UO_2. Also the substrate geometry (size and form) is important in the process. Kernels should be dense, spherical with a diameter distribution very narrow.

6.1 HfO_2 kernels

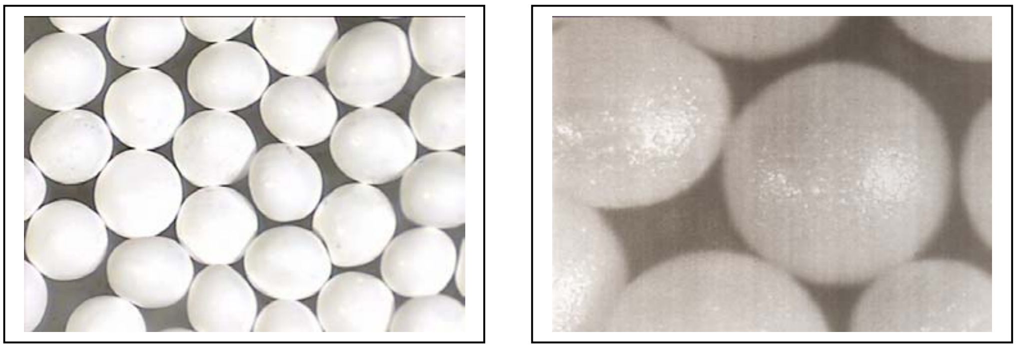
Concerning simulant kernel, BRACE, a German company has been identified. This company seemed to be the potential supplier of these kind of kernel. Indeed, the director of Brace is a former nuclear specialist, responsible in the 80's in fuel HTR kernels fabrication (elaboration, coating…) at Nukem. After that the programs in Germany stop, all the installation of Nukem was dismantled and most sold in China in the years 92-95.

In spite of the contacts developed at the beginning of the project, the numerous samples examined did not answer to our specifications. However, a thermal treatment high temperature (1700 °C / 4h) under air realised on samples elaborated by the Sol-Gel process, allowed:

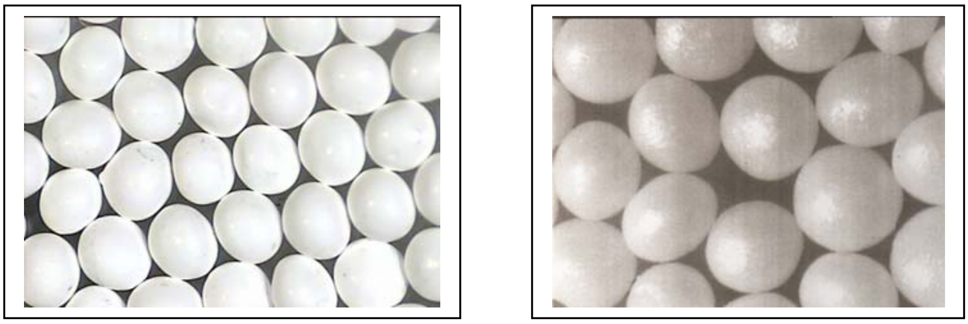
- to specify to Brace the size of microspheres to be taken into account in the process of elaboration,
- to know the density of the material after sintering,
- to verify the behaviour of the material in temperature.

HfO_2 stabilised with Y_2O_3 or MgO was necessary to insure a good mechanical behaviour during SiC deposit process (~ 1600 °C).

We can see the aspect of the balls before (figure 5a) and after sintering (figure 5b).



Lot T2508-1 **X 16** **X 72**



Lot T2508-2 **X 16** **X 32**

a : calcined at 800°C **b : sintered at 1700°C under air**

Figure 5. Balls elaborated by Sol-Gel process.

The table below gives the measures of diameters before and after sintering.

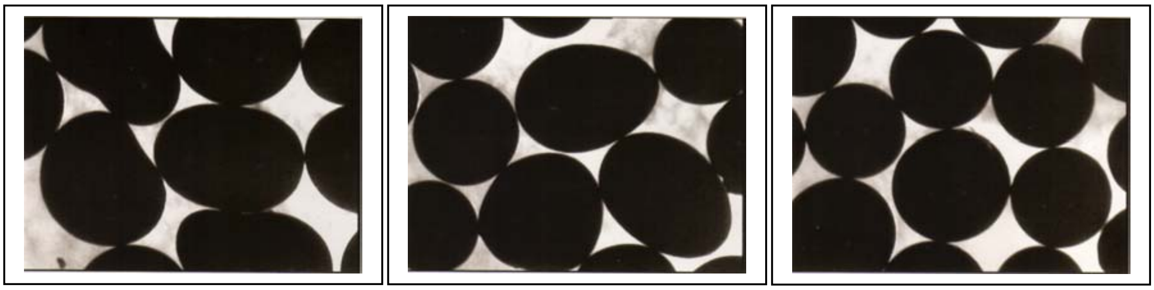
Sample	Before sintering				Après sintering	Retreat (%)
	Taille inf. (µm)	Volume %	Taille sup. (µm)	D Moyen. (µm)	D Moyen. (µm	
T2508-1	647,41	0,06	754,23			
	754,23	9,29	878,67			
	878,67	85,37	1023,66	**944**	**605**	**35,9**
	1023,66	5,2	1192,56			
	1192,56	0,07	1389,33			
T2508-2	647,41	0.02	754,23			
	754,23	2.63	878,67			
	878,67	74.48	1023,66	**982**	**623**	**36,5**
	1023,66	22.35	1192,56			
	1192,56	0.53	1389,33			

It is evident that the specifications like sphericity and size distribution are not respected. The average diameter measured after sintering is about 600 µm with however an important retreat.

The density measured by He pycnometry is 9.07 ± 0.02. Indeed, the addition of Y_2O_3 (5,23 weight %) for the stabilisation and Al_2O_3 (2,23 weight %) to improve the sintering entailed a density weaker as regard as pure HfO_2. However, as we can't know exactly the theoretical density of the material considering the various additions and the density data, variable according to the literature, the calculation (statistically incorrect) made from the rule of mixtures gives a value of 98 % with regard to the theoretical density.

6.2 ZrO_2 kernels and first deposit tests

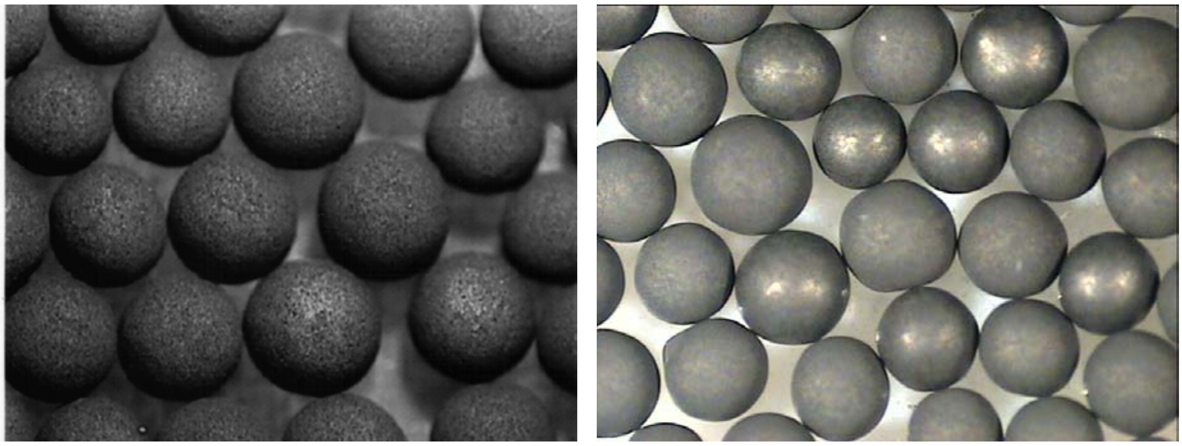
Further to the problem of supply in HfO_2 balls, first tests were realised on ZrO_2 kernel with a density of 3.67 from SEPR (European Society for Refractor Products). Figure 6 shows the various batches obtained after a selection shape on a small vibrating table.



→ 1st step **→ 2nd step** **→ 3 rd step**

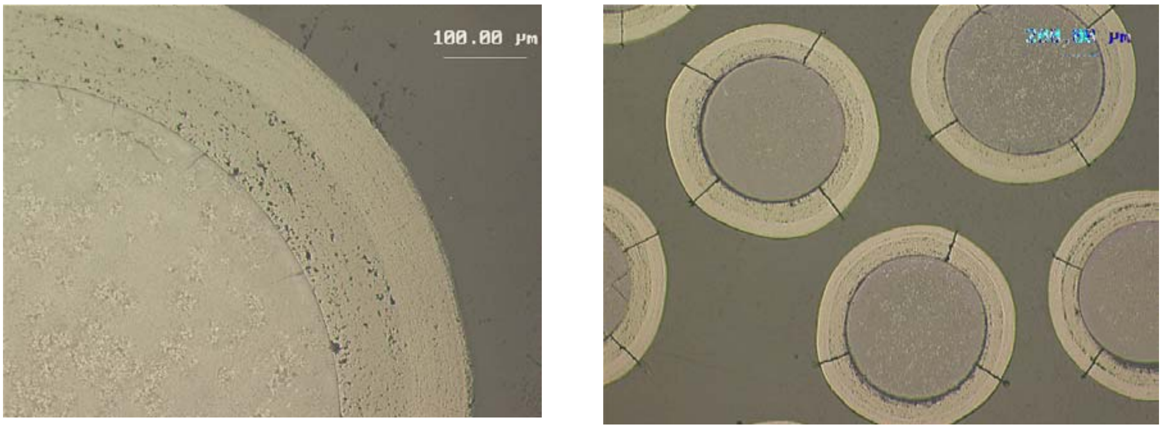
Figure 6. ZrO_2 balls from SEPR showing the selection form.

Porous PyC deposit presents a surface aspect with orange peel effect (figure 7a) while the deposit of dense PYC is smooth and brilliant (figure 7b). The thickness was approximately 90 µm for the porous deposit and 70 µm for the dense coating (figure 8a). Problems of fissuration appear in layers (figure 8b) linked probably to the difference of expansion coefficients between carbon and zirconia but also by the phase transformation of pure zirconia (~1170°C) in our deposit conditions.



a) **b)**

Figure 7. PyC deposits on ZrO_2 kernel.

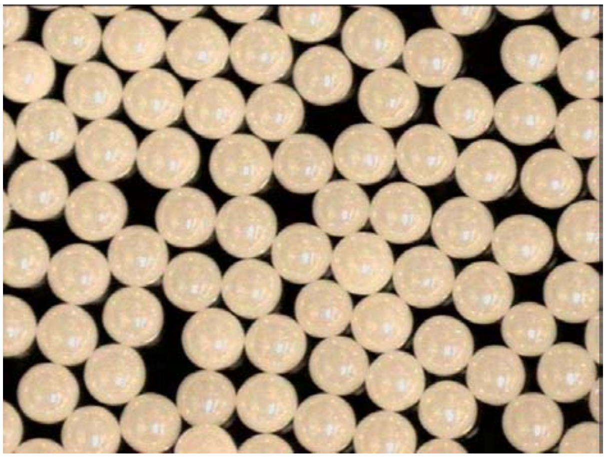


a) **b)**

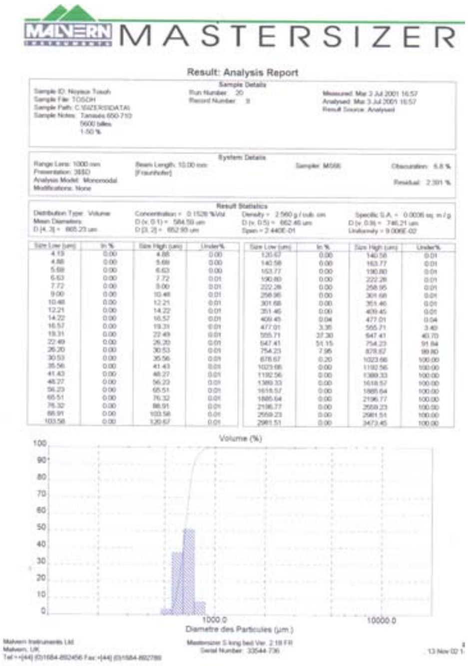
Figure 8. View of particles cross section.

6.3 ZrO_2/Y_2O_3 Kernels

Tests have been finally optimised on ZrO_2-Y_2O_3 (95/5 weight %}material from TOSOH, with a relatively high density and a perfect spherical form (see figure 9a). As the fluidised bed process depends on the ~~density and~~ the square diameter of kernels, and considering that the density of TOSOH kernels was 6.1 (measured by He pycnometry) instead of 10 for UO_2, the average of kernels diameter was voluntarily calibrated at 650 ± 80 µm (see report figure 9b).



(a)



(b)

Figure 9. (a) ZrO_2/Y_2O_3 kernels from TOSOH.
(b) Diameter analysis report.

7. COATING TESTS

7.1 PyC deposits

The tests have been realised, depending on the deposition, by varying:

- temperature reaction controlled by a pyrometer
- active gas (C_2H_2 or C_3H_6) fraction.

The figure 10 shows, concerning PyC porous deposit, that the density is depending on the fraction gas (C_2H_2) principally. For dense PyC, it is the temperature which is the most important to obtain a pyrocarbone with a higher density. These results are in concordance with the literature [5], knowing that it is possible to deposit dense pyrocarbone with another gas like CH_4, but at higher temperature, typically 1900°C.

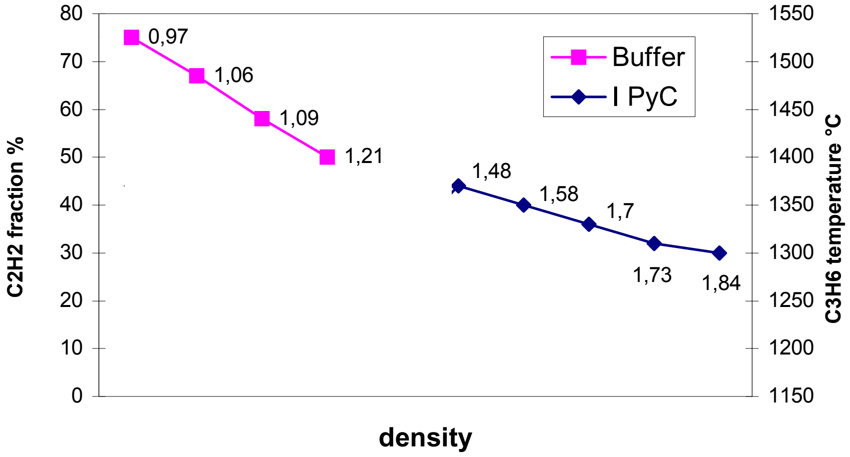


Figure 10. Effects on PyC coating process of varying:
- the gas (C_2H_2) fraction
- the temperature with C_3H_6

The density values was respectively measured and compared by WLS and FCF methods. The tables (figure 10) summarises the results obtained with the two methods; floatation method has permitted to measure densities from 1.67 (T= 40°C) to 1.95 (T=16°C) with pure Iodoethane or mixed Iodoethane/xylene.

Layers	Thickness	Density	Coating rate µm/mn	Gas fraction %
Buffer	**97**	**0.97**	**~ 28**	**75**
Specification	*95*	*< 1.05*	*16.6*	*65*
Min-max	*75-115*		*8.3-33.6*	*60-70* *
IPyC	**44**	**1.84**	**~3.5**	**22.8**
Specification	*40*	*1.9*	*> 3.0*	*25*
Min-max	*30-50*	*1.8-2.0*	*2.0*	*20-25*

Batch coating	ZP 12 buffer	ZD 13 *I PyC*	ZD 14 *Buffer + IPyC*	Method
Thickness (xx ± ?)*	97	39	44	WLS
Density (xx ± ?)*	0.97	1.94 1.95	*1.84* *?*	WLS FCF *

Figure 10. Table given results according to the specifications.

3 batches (ZP12, ZD13 and ZD14) were carried out and dispatched to JRC/Petten to compare layers thickness with a X-Ray method (deliverable 17). A cross section of the particles (ZD 14) shows the different coatings (figure 11):

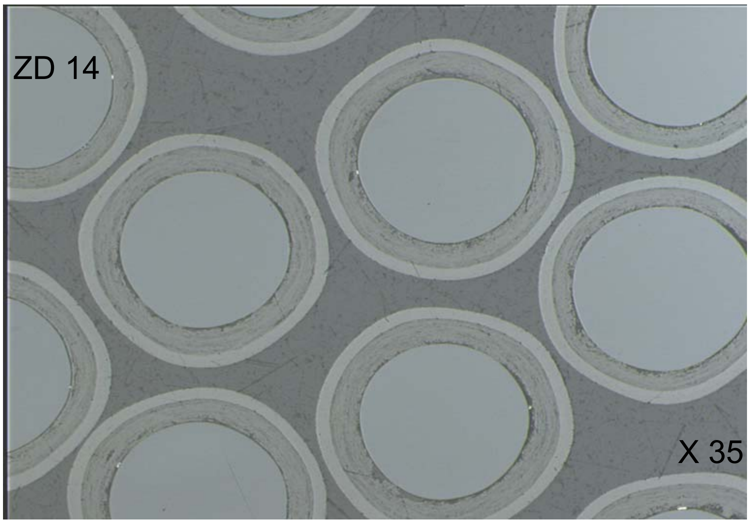


Figure 11. Cross section particles with buffer and IPyC coatings.

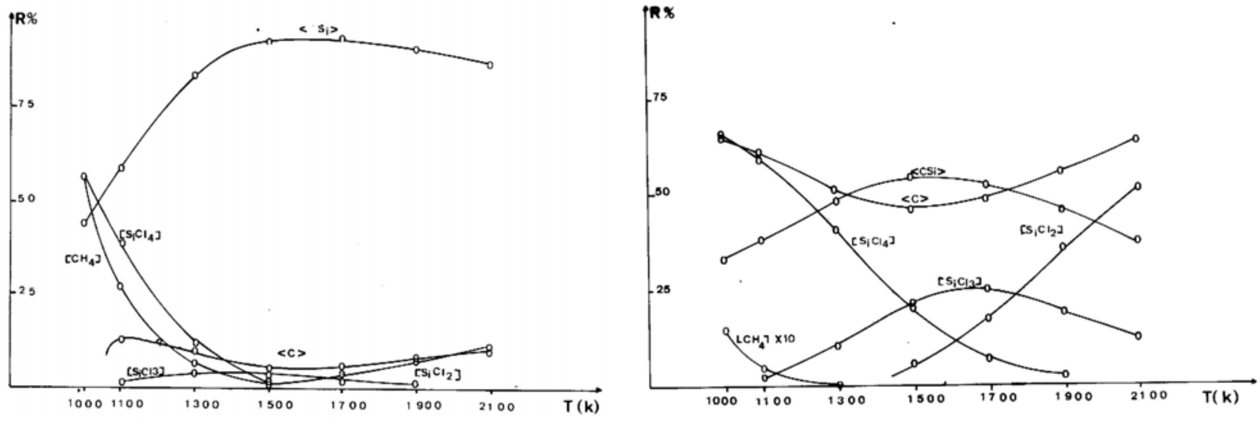
7.2 SiC deposit

Methyl TriChloro Silane (MTCS: CH_3SiCl_3) is an available industrial product; it is notably used in the industry of silicones. Since the beginning of 1960's, the studies concerned mainly the definition of the thermodynamics and kinetics conditions of manufacture allowing to answer to the evolution of fuel wished performances.

A device, used in the 1970's has been restored and renewed (figure 12).

Figure 12. MTCS (SiC precursor) device.

CH_3-$SiCl_3$ is liquid at room temperature. The transport of gaseous precursor is obtained by barboting with H_2 to avoid deposit of free carbon as we can see when Ar is used (figure 13).



P_0 CH_3-$SiCl_3$ = 0.10 atm-P_0 H_2 = 0.90 atm **P_0 CH_3-$SiCl_3$ = 0.10 atm-P_0 Ar = 0.90 atm**

Figure 13. Thermodynamic comparative analysis with CH_3-$SiCl_3$ barboting in H_2 and Ar. Efficiency evolution with the temperature for a defined composition.

The CH_3-$SiCl_3$ flow was controlled by flowing H_2 through it at fixed pressure and temperature gases.

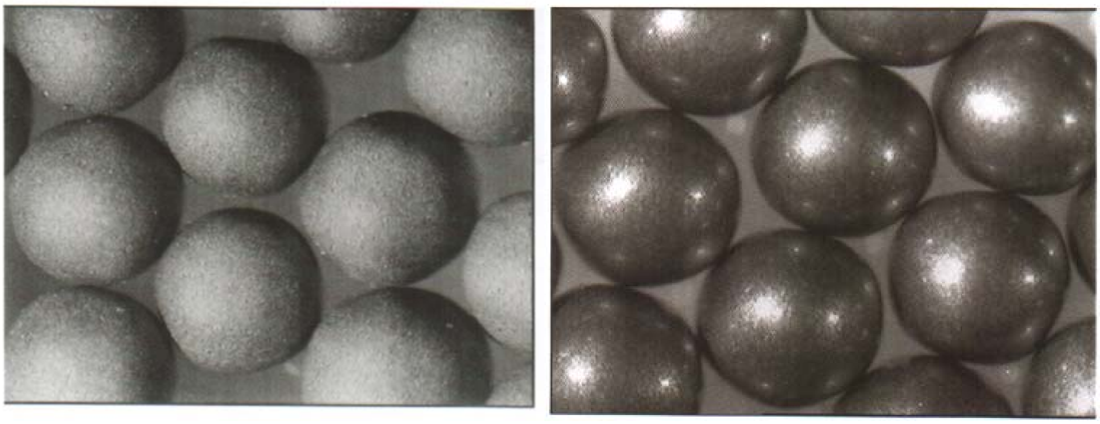
The coating parameters chosen for the tests were temperature, total flow of reactant and product gases, and H_2/CH_3-$SiCl_3$ ratio near the given specifications (in theory 20-30). The temperatures examined were 1500, 1550 and 1600°C, with three different H_2/CH_3-$SiCl_3$ ratio as it is showing in the table figure 14.

The values of efficiencies obtained are high and closed to thermodynamic results.

A smooth surface and metallic aspect with an efficiency of 93 % were observed at T =1600 °C by varying the deposition speed compared with an other aspect obtained at 1500 or 1550°C (figure 15). We could supposed that a metallic aspect would seem to represent better deposit conditions.

Test N°	14	15	16	17	18
Temperature °C	1600	1600	1600	1550	1500
Ratio H_2/CH_3-$SiCl_3$	35.1	24.1	20.5	20.5	20.5
Efficiency %	88	92.1	93	93.1	93.6

Figure 14. Conditions and efficiencies of SiC deposit.



$T_{deposit}$: 1500-1550 °C

$T_{deposit}$: 1600°C

Figure 15. Exterior aspect of SiC particles.

7.3 X-Ray analyse

Nevertheless the graph obtained on 1600°C deposit, figure 16, underlines the presence of two main SiC phases. One has a β cubic structure and an other one which could be SiO_2 of hexagonal structure (worrying considering our reducing conditions of deposit) and\or may be SiC disordered α hexagonal structure. However, no carbon free were observed.

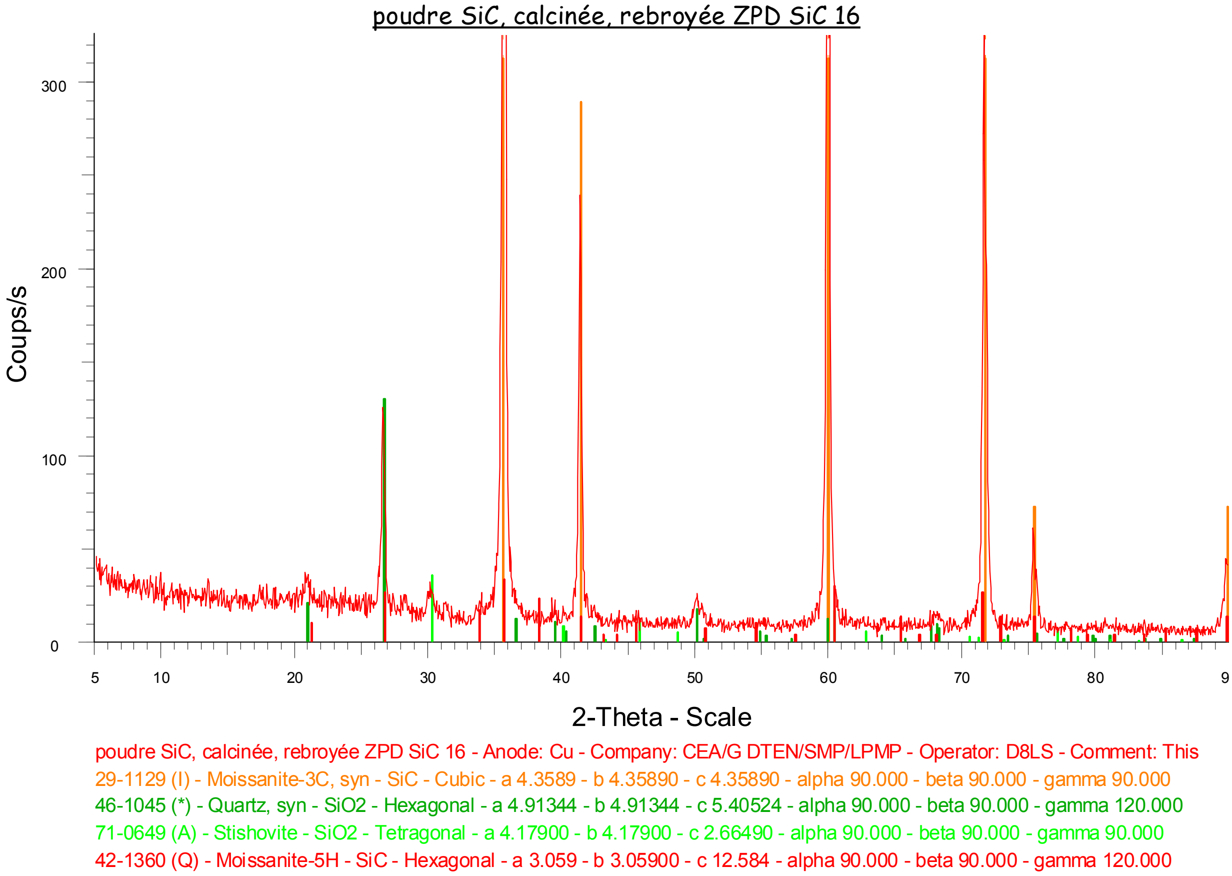
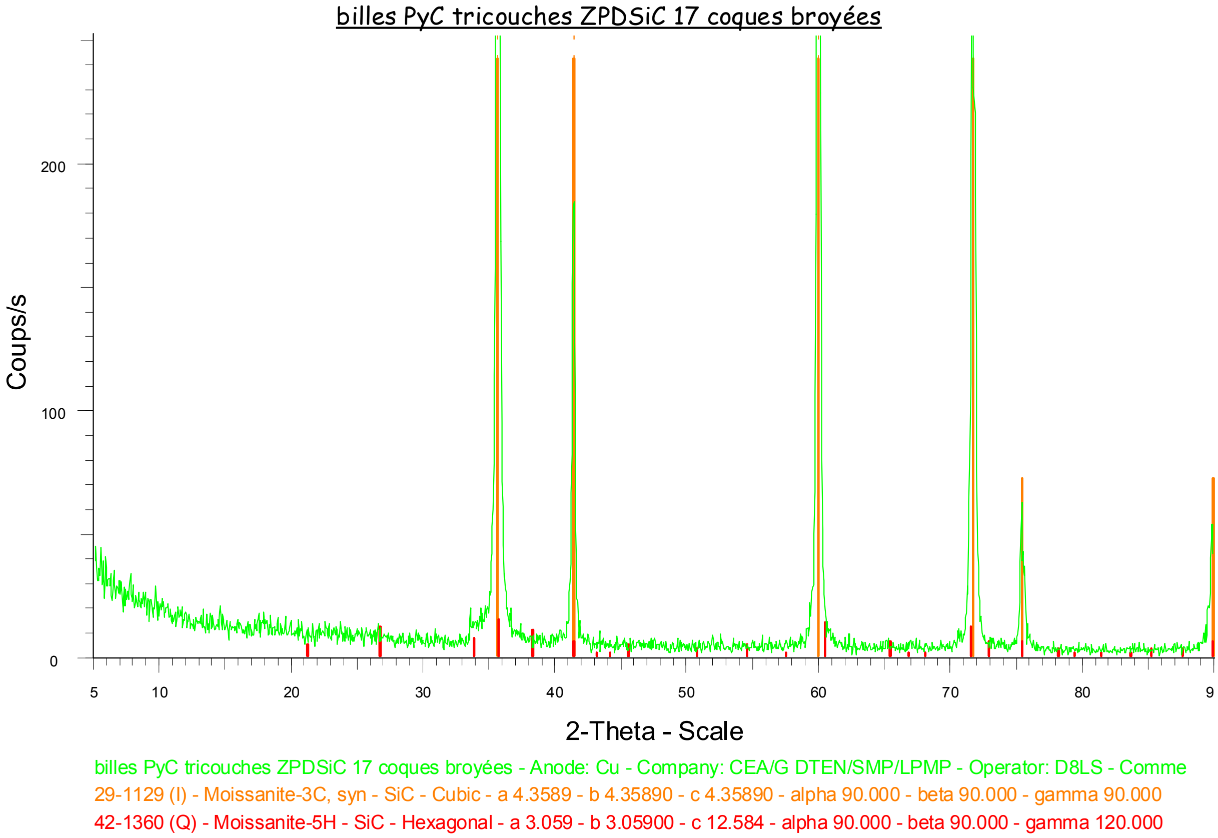


Figure 16. X-Ray graph of SiC deposit n° 16.

To stop on these hypotheses, it would be necessary to make EDS analysis and images in retro diffuse mode on a massive layer. We can note that the same results were observed on sample number 15. In the aim to remove this doubt, we realise analysis on sample obtained at 1500 and 1550 °C (figure 17). We can see that the graphs are identical and correspond to SiC cubic phase. A small supplementary peak seems to be attributed to SiC hexagonal, but on non account, spectrums look like sample number 16. We can supposed that the apparent of SiO_2 phase is credibly a disordered phase of 2H hexagonal SiC and that a phase transformation β→ α appears near 1600°C.



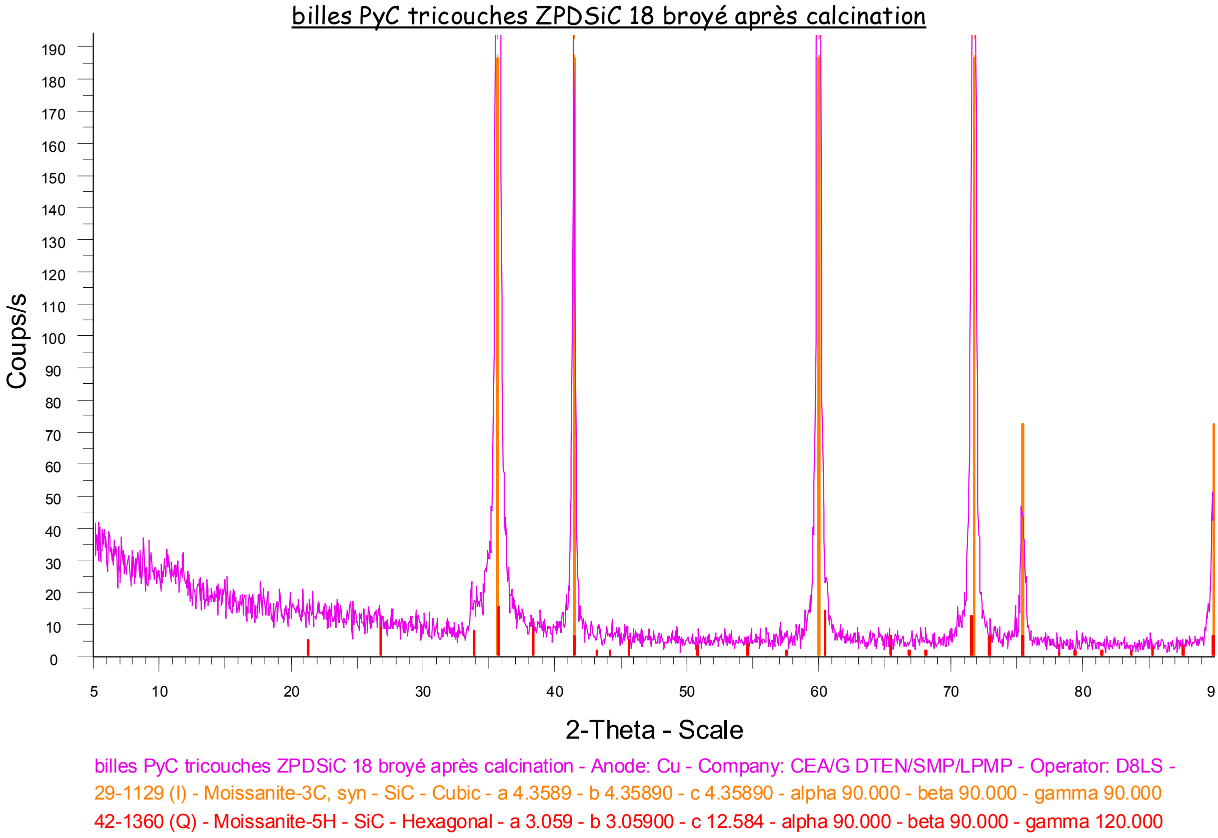


Figure 17. X-Ray graph of SiC deposit n° 17 and 18.

7.4 Physical characteristics

Physical characteristics like thickness and density were measured (samples 16 and 18) by Laser light Scattering and floatation method. The table figure 18 summarises the measures realised. The precision of the measures should be confirmed and compared with others methods in development besides.

We can see on figure 19, that particles are intact after the various phases of deposit. No fissuring is observed on many particles taken at random, what proves a good behaviour in temperature. Cross sections show homogenous thickness of the deposit and variable densities obtained according to the type of deposit.

Test number	16			18			Methods		
layer	**buffer**	**IPyC**	SiC	**buffer**	**IPyC**	SiC			
Thickness	**91**	**45**	**30**	**94**	**40**	**38**	LS	LS	LS
Density	**1.03**	**1.89**	3.202	**0.87**	**-**	>3.2	LS	LS	FCF

Figure 18. Measurement of the coatings thickness and density.

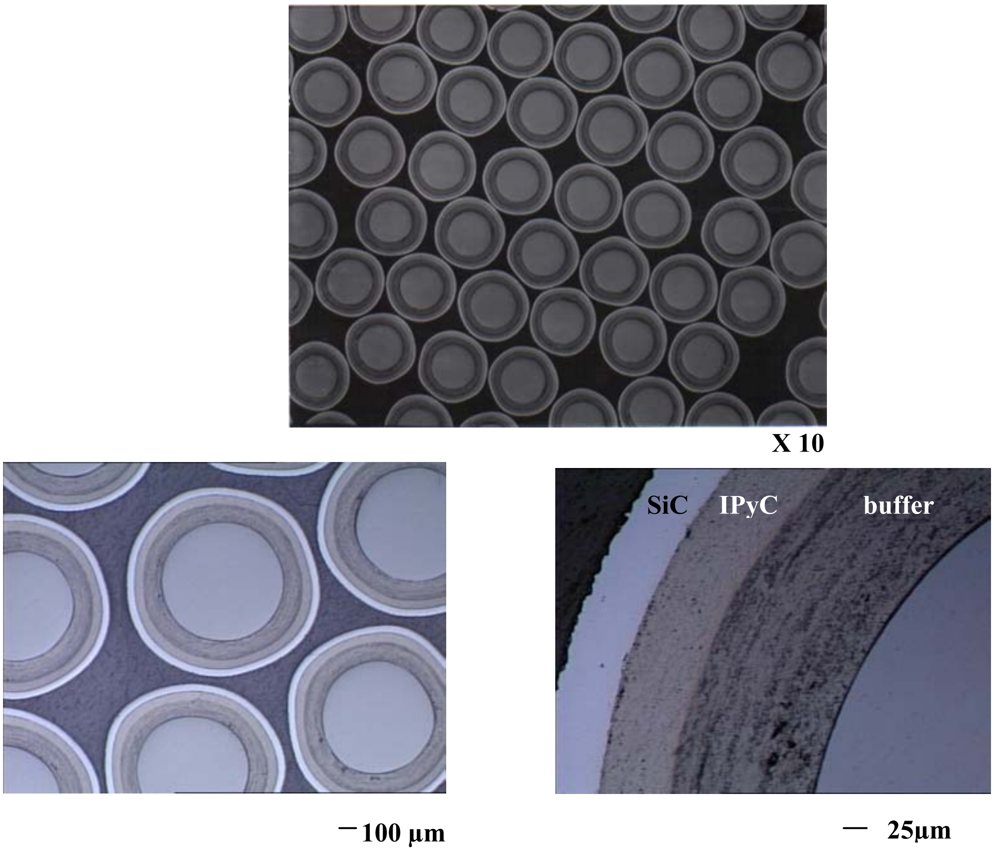


Figure 19. Cross sections of PyC/SiC particles.

9. CONCLUSION

First good “TRISO” particles were obtained with zirconia kernels stabilised with yttria. The first characterisation results confirm that the specifications are respected. Although the envelope of the particle is not completely ended, the major part of the work was realised.

The conditions of deposit for pyrocarbone according to the fixed density were optimised. They depend in the case of the buffer on the fraction of C_2H_2 in the mixture and in a lesser degree of the temperature of deposit. Conversely, to obtain a dense pyrocarbone, it is the temperature which is the parameter the most mattering with C_3H_6 use as gas precursor. The deposit of silicon carbide, should be made at higher temperature to obtain the cubic phase β. However, it would seem that the deposit should be realised in a temperature lower that 1600°C, to avoid the formation of SiC α.

In the future work, others tests on SiC have to be realized in the aim to eliminate completely alpha phase proportion by varying the temperature. OPyC layer will be deposited and optimised to finalise the TRISO coating process.

Finally, a review on ZrC as a new coating material and thermodynamic calculations are on progress at CEA/Grenoble. A comparison will be done between iodide, chloride and bromide of zirconium which are 3 potential precursor of ZrC.

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