New Techniques Dedicated to the Characterization of Future Nuclear Fuels

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ABSTRACT

The SPUA (Plutonium Uranium and minor Actinides Service), located in CEA (French Atomic Energy Commission) at Cadarache, is in charge of the elaboration and characterization studies of as-fabricated nuclear fuels, present or future, as well as actinides (Am, Cm) transmutation targets.
Conventional techniques (in glove-boxes environment) are used to make uranium and/or plutonium oxide fuels and different equipments are dedicated to their microstructural and thermo-mechanical characterization.

GCR (Gas Cooled Reactor) type needs innovating concepts such as new fissile materials (nitrides or carbides) or different fuel geometries (particles or fibers most likely inserted in spherical or hexagonal elements). Consequently, current elaboration and characterization techniques will evolve to fulfill these new requirements.

The SPUA is already working on HTR (High Temperature Reactor) particles elaboration and is contributing to new GCR's fuels choice by studying innovative elaboration processes. At the same time, we are investigating new microstructural characterization methods and different thermal properties determination devices. Thanks to that, we will be able to reach the intrinsic properties of fuel materials before irradiation. These techniques are developed with keeping in mind to be compatible with hot cell's post irradiative examination (PIE).

In the presentation, we shall provide a description of the currently investigated techniques and devices for unirradiated future fuels and their use in hot cells will be discussed.

KEYWORDS : future nuclear fuels, characterization, thermal properties

1 Introduction

The SPUA (Plutonium Uranium and minor Actinides Service), located in CEA (French Atomic Energy Commission) at Cadarache is in charge of the elaboration and characterization studies of as-fabricated nuclear fuels. Thus, to fulfill the request of the industrials (COGEMA, EDF, FRAMATOME), researches are made on new fabrication processes to obtain advanced microstructure fuels which can be able to reach high burn up. Their characteristics have then to be evaluated and compared with current fuel ones to confirm that they are not reduced.
Moreover, GCR (Gas Cooled Reactor) type needs innovating concepts such as new fissile materials (nitrides or carbides) or different fuel geometries (particles or fibers most likely inserted in spherical or hexagonal elements). Consequently, current elaboration and characterization techniques will evolve to carry out these new requirements. Therefore, the SPUA is already working on HTR (High Temperature Reactor) particles elaboration and is contributing to new GCR's fuel choice by studying innovative elaboration processes. At the same time, we are investigating new microstructural characterization methods and different thermal properties determination device.
After a quick overview of innovative fuel elaboration processes, all investigated techniques will be presented. Their compatibility with hot cell's post irradiative examination (PIE) will be also discussed.

2 Elaboration processes

To date, Power Water Reactors (PWR) or Liquid Metal Fast Breeder Reactors (LMFBR) used fuel pellets elaborated by classical powder metallurgical route. The new type of reactors will need another fissile materials and fuel geometries, requiring innovative elaboration processes. For less or more long-term R&D programs, the SPUA is working on HTR fuel particles elaboration and is contributing to new GCR's fuel choice. Since the GCR's fuel definition is still on progress, we will only present in this paper the work we are performing on HTR fuel.

2.1 HTR fuel description

Generally, around the world, the HTR fuel is based on spherical coated particles inserted in graphite blocks element named compact for the US concept and pebble for the German one. Classical dimensions of US cylindrical compacts are about 1 to 2-cm-diameter and 5-cm-long. The overall diameter of the German spherical fuel element is 6 cm, with a 0.5-cm-thick fuel-free shell.
The HTR coated particle consists of a UO_2 fuel kernel that is surrounded by a porous pyrolytic carbon buffer layer, an inner dense pyrolytic carbon layer (IPyC), a silicon carbide layer (SiC) and an outer dense pyrolytic carbon layer (OpyC). The diameter of the UO_2 kernel is about 500 µm whereas the diameter of the overall coated particle is about 900 µm. Figure 1 shows a metallographic section of a TRISO-coated UO_2 particle and a German pebble fuel element.
Each layer in the TRISO particle design plays a role in fuel performance and fission product (FP) retention. The buffer layer provides a void volume for gaseous FP and accommodates kernel swelling. The dense IPyC reduces tensile stress on SiC and acts as diffusion barrier to metallic FP. The SiC layer ensures leak tightness to metallic FP during normal and accidental situations. The dense OPyC layer reduces tensile stress on SiC as IPyC and provides bonding surface for matrix material.

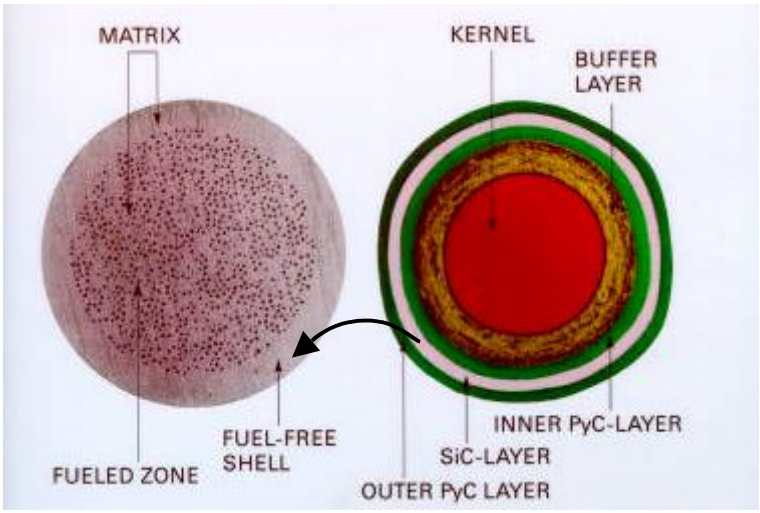

Figure 1 : *Cross-section of a pebble fuel element and HTR coated particle, source [1]*

2.2 HTR fuel fabrication process

At present, the SPUA is already working on HTR particle elaboration and is now able to produce UO_2 fuel kernel. It is produced by a sol-gel method named the Gel Supported Precipitation which is based on external precipitation of uranyl nitrate supported by a polymeric chain and has been largely studied in the past [2]. Spherical droplets of a broth containing uranyl nitrate are produced by a vibrational dropping technique and fall in a NH_4OH gelation bath. These droplets are aged to improve internal structure, then are washed to remove nitrate. Following the drying and calcining steps, a reduction-sintering stage is completed to produce highly dense UO_2 kernels. The coating of the kernels is performed by Chemical Vapour Deposition (CVD) in fluidized beds [3]. Pyrolysis of adequate hydrocarbons and SiC precursor leads to the formation of the final coated fuel particles. R&D of CVD coating takes place, for the moment, at CEA/Grenoble.

In parallel to this innovative process studies, the SPUA is also investigating new characterization methods. Thus, to fulfill the needs of the modeling, different properties before and after irradiation have to be evaluated. Presently, we are studying different HTR fuel characterization methods with keeping in mind to be compatible with the future GCR fuels and also with hot cell's Post Irradiative Examination (PIE).
The SPUA is working on microstructural and thermal characterization whereas mechanical characterization and pyrocarbon anisotropy are being studied by another service located in CEA Pierrelate (DTE/STME).

3 Characterization methods

3.1 Microstructural characterization

As it has been pointed out by German experience [3], irradiation performances of HTR fuels impose requirements on HTR coated particles, such as a low standard deviation of kernel diameter and sphericity, a close control of coating thickness. In order to provide a quality control method for coating and particles specifications, the potentialities of the image analysis associated to optical microscopy have been evaluated for reaching the kernel sphericity (D_{max}/D_{min}) and size, and the layer thickness of the different coatings. The possibility to extend the characterization to the porous volume fraction (feature theoretically accessible by image analysis) will be viewed in further steps.

3.1.1 Description of the method

As any method involving image analysis, the overall procedure we developed [4], can be decomposed in four main steps which are :

a- sample preparation,
b- image acquisition
c- grey level image treatment and binary image analysis,
d- parameters measurement associated to significance level.

Depending of the desired parameters (kernel sphericity and diameter or layer thickness of coated particles), the sample preparation consists either to deposit the kernels on transparent support (acquisition made in transmission mode) or to polish carefully HRT coated particles (acquisition made in reflexion mode), once vacuum embedded. The image acquisitions are made via a CCD camera relied to an optical macroscope LEICA M420. The choice of the magnification, function of the size of the analysed beads, is taken in order to have a minimal precision of 1% on the measured parameters.

The digitised images are automatically analysed with a procedure, which has been especially developed for this kind of measurements on a commercial software (AnalySIS).

The measured parameters are the equivalent circle diameter (ECD) for the kernel size, the ratio maximum Feret diameter/minimum Feret diameter for the kernel shape. The layer thickness of each coating is deduced from surface measurement of the latter intercepted by the polished plane. In order to take into account that the polished plane may be different from the diametral one, a correction is applied to the measured layer thickness that allows us to determine the real thickness of each layer.

Finally, the image analysis provides us the arithmetic mean and standard deviation of the relevant parameters. And assuming a gaussian distribution of the experimental values, the Student law enables us to estimate the number of beads or kernels to be analysed such that a distinct statistical significance is guaranteed.

3.1.2 Image analysis applied to simulant material

Image analysis, as described above, has been applied to characterize a batch of simulant kernels (ZrO_2) and another one of simulant particles (composed of ZrO_2 kernel coated with buffer and intern dense PyC layers). The resolution for the analysis of kernels is 5.4 µm and the one for the layer thickness determination is 1 µm. The results are given in Table 1. The number distribution of all the measured parameters can also be printed

Statistical number	**ZrO_2 simulant kernels**		**Simulant HTR particles**	
	Diameter ECD (µm)	D_{max}/D_{min}	Buffer PyC thickness (µm)	Inner dense PyC thickness (µm)
Arithmetic mean	646.3	1.049	94.6	42.8
Standard deviation	17.7	0.014	8.9	2.2

Table 1 *: Simulant kernel size and shape and layer thickness of simulant particles*

With those statistical numbers, it is possible to define a significance level of the measure. For example, if one wants to estimate the layer thickness with a relative precision of ± 1%, it appears necessary to analyse more than 300 particles (530 particles) in order to reach a confidence interval of 95% (99%).

3.2 Measurement of pyrocarbon anisotropy.

In the case of pyrolytic carbon, it is known that most of the physical properties change with their texture. Generally for mechanical application, in the field of carbon composites, one search to produce strongly anisotropic pyrocarbons. On the contrary, in the peculiar case of HTR applications, isotropic pyrocarbons are required because of the spherical geometry of the HTR fuel. The criteria 'degree of pyrocarbon anisotropy' is essential to be characterized specially for IPyC and OpyC before irradiation, to be sure that HTR coated particles respect the specification and also after irradiation, in order to understand the influence of in-pile conditions on the pyrocarbon structure modification (sintering, orientation of graphitic plans, etc).

Different methods have been developed to measure anisotropy. Most are based on X-Ray diffraction on flat disks [5] or directly on the spherical layers of particles [6]. The others involves optical methods [7,8,9,10] by measuring the reflecting power anisotropy. Those latter have been largely studied in the 70-80's so that optical method is becoming the international reference for characterizing HTR pyrocarbons. To simplify, it is based on the determination of an "optical anisotropy factor" which is defined as the ratio of maximum-to-minimum intensity of the reflected polarized light by rotating the stage on specified field of the sample. The field is to be defined precisely, it is generally between 5-µm-large to 15-µm-large.

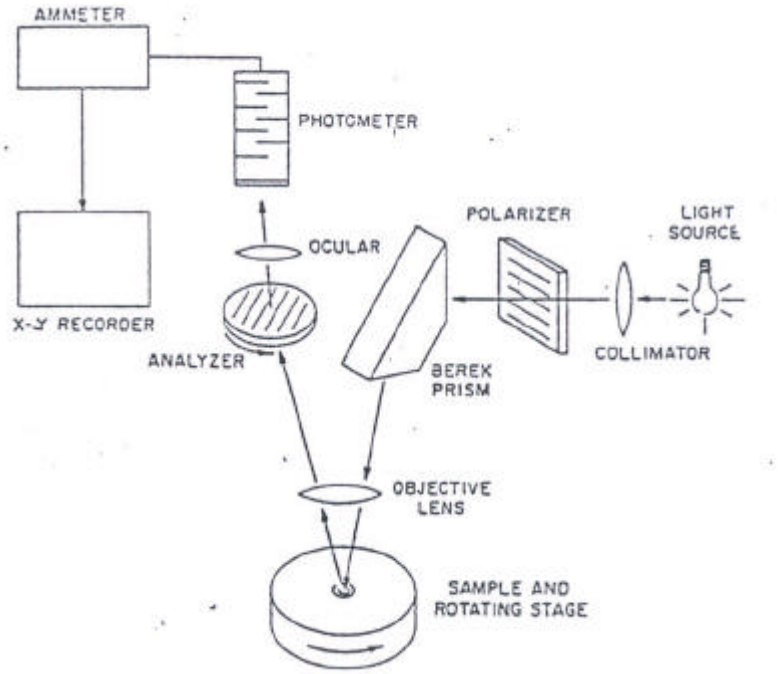

Figure 2 *: Schematic showing principal elements of microphotometer [7]*

In the past R&D, as shown in the sketch in figure 2SEQARABE, the reflected and polarized light beam was analysed by a photomultiplier tube (after having selected a wave length). Taking account of electronic progress, assessment of the use of a spectrophotometer is undergone by CEA/Pierrelatte and Cadarache in collaboration with LCTS Bordeaux. The main advantage of the spectroPM is that all the visible spectrum can be measured whereas before one was obliged to work with a fixed a value of the wave length. Further studies will concern the development of the microscope spectrophotometer and the determination of all

experimental parameters (i.e. size of the beam window, of the optimal wave length, effect of magnification,…) ruling the measure of pyrocarbon anisotropy by optical reflectance.

3.3 Thermal characterization

In order to anticipate the thermal behavior of a component, thermal conductivity is to be determined. It is necessary to predict the temperature of the pellets and so, to avoid any core fusion.
More often the thermal conductivity is deduced from this equation :

$$\ddot{e} = \rho\, a\, Cp$$

With :

λ	:	Thermal conductivity [$Wm^{-1}K^{-1}$]
ρ	:	Density [kgm^{-3}]
a	:	Thermal diffusivity [m^2s^{-1}]
Cp	:	Heat capacity [$Jkg^{-1}K^{-1}$]

To obtain the thermal conductivity, we have to measure thermal diffusivity and heat capacity. To date, the techniques used have been designed to evaluate uranium and plutonium fuel pellets properties. Thus, the SPUA possesses experimental device (named PROTEE, picture on figure 3) installed in a glove box that can be used in two configurations allowing the measurement of either heat capacity and thermal diffusivity. Thanks to this device, a recommendation of Mixed Oxide fuel have been evaluated [11]. This technique requires disk samples about 6 to 10 mm diameter and 1.5 to 4 mm thickness. Then, after some preparation sample, the HTR or GCR compact's thermal properties will be able to be measured by these conventional techniques.

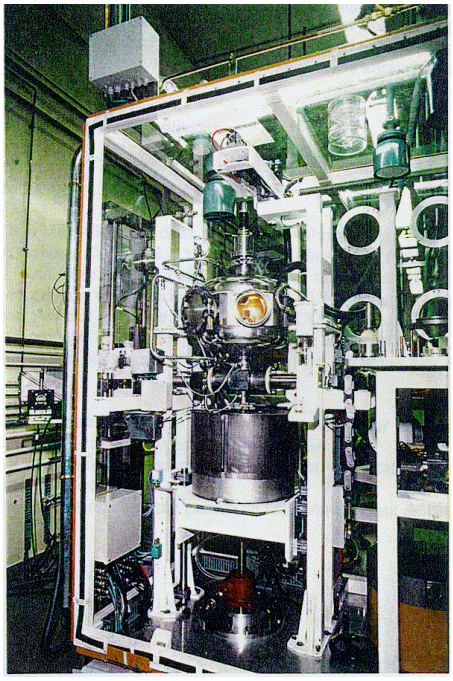

Figure 3 : *PROTEE device*

3.3.1 Compact's thermal characterization device description

The first configuration of PROTEE device is an original drop calorimeter which allows the enthalpy measurements to be carried out. The sample suspended on a metallic thread is heated by high frequency induction. The temperature measurements can be performed up to 3000 °C. But, because of bichromatic pyrometers techniques used to measure sample

temperature, the lowest temperature is limited to 400 °C. The thread is then released into a highly sensitive thermopile which registers the energy restored until return to the room temperature. Then, Enthalpy H = f(T) is calculated and specific heat capacity can be deduced by the following relation : $Cp = \frac{dH}{dT}$. The principle is resumed in figure 4.

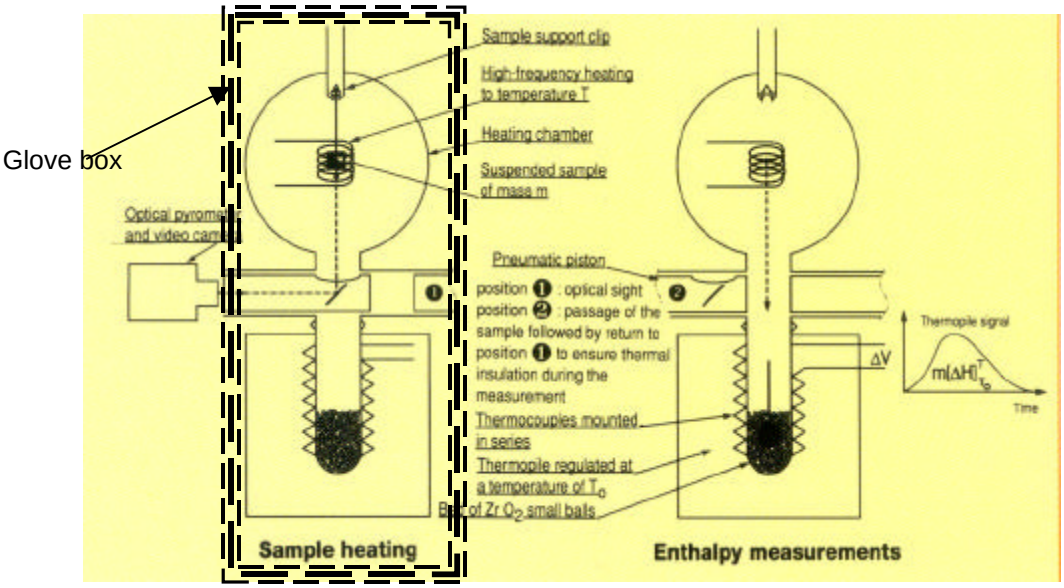

Figure 4 ***:*** *Drop calorimetry configuration*

The second configuration allows the thermal diffusivity measurement. The principle is presented in figure 5. A laser flash is sent onto one face of the sample. The thermal response is registered on the other face. The signal is directed onto an infrared detector, then amplified and analyzed to determine the thermal diffusivity.

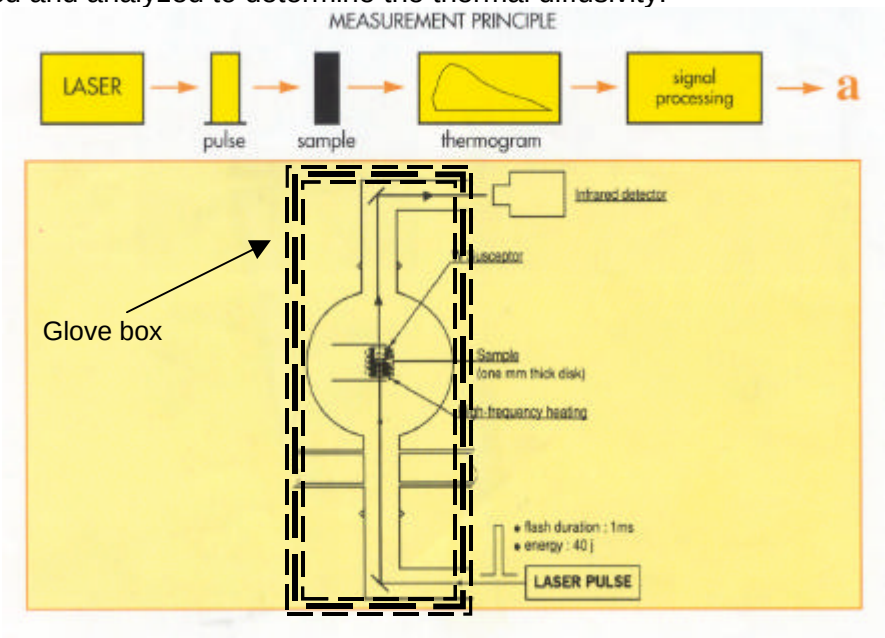

Figure 5 ***:*** *Thermal diffusivity measurement configuration*

For the same reasons as in other configuration, the measurements can only be performed from 400 °C up to 3000 °C.

3.3.2 HTR fuel particles thermal characterization

In order to have a better understanding of this complex materials and of its behavior, it is important to know the physical parameters not only at a macroscopic scale but also for each

constituent at a microscopic scale. Photothermal experiments are particularly suitable to determine thermal diffusivity at different scales, from the micrometer to the millimeter, simply by varying the modulation frequency [12]. Thus, one technique we are studying is thermoreflectance microscopy. The method consists in photothermal effect detection which allows a non destructive and without contact thermal diffusivity measurement. This technique is born in United States in 1985, and since has been developed in different French laboratories. A sketch is given in figure 6.

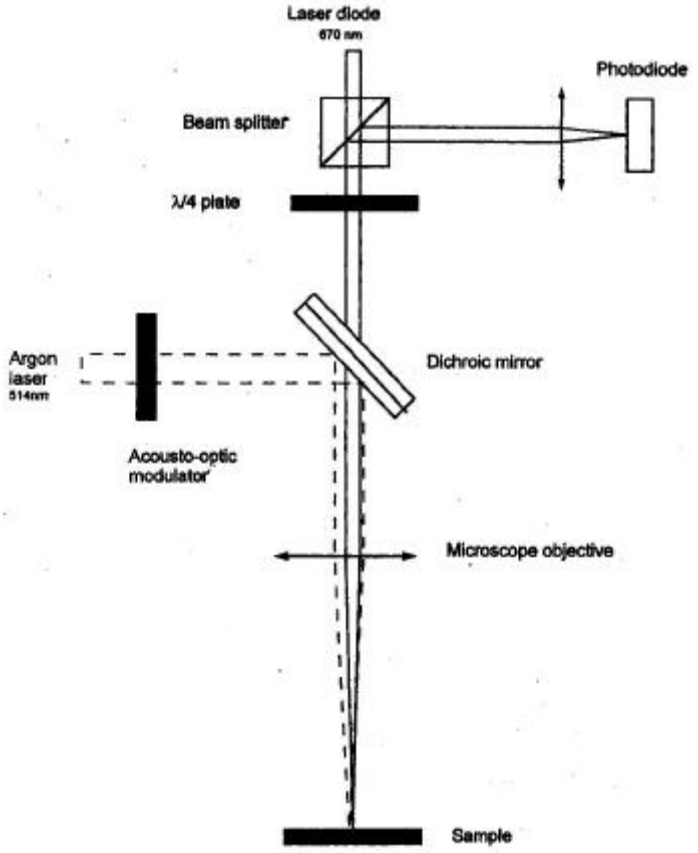

Figure 6 : *Sketch of the photoreflectance microscope*

A photothermal experiment involves the “contribution” of :

- the illumination of the sample with a pulsed or modulated pump beam;
- the detection of the surface or volume temperature variations related to the transfer of absorbed radiant energy into heat.

Two different lasers are used to perform the measurements : one (Argon laser) is used as heating laser beam and the other one (diode laser) is used as detection laser beam. Both are focused through optical microscope to perform very local measurements. The thermal diffusivity measurements requires the heated area to be thoroughly explored, the extension of the latter being related to the diffusivity. After a modeling taking into account any medium in which the heat can diffuse as well as geometrical parameters of the experiment, the thermal diffusivity can be extracted with a precision often better than 5 %.

This technique has specially been developed in France by ESPCI (Paris school of physics and chemistry). Also, as part of a training [13], this technique has been employed to measure uranium dioxide’s thermal diffusivity at room temperature. The experimental measured value was in good agreement with literature data obtained by conventional methods such as laser flash.

Recently, at CEA Ripault, this technique is developed to realize thermal diffusivity measurements up to 1000 °C.

We foresee to realize measures on inactive particles to confirm the feasibility of the photothermal method before SPUA investing in this equipment in order to be able to measure thermal diffusivity of active fuel particles.

4 Conclusion

In the framework of innovative fuel concepts (HTR or GCR), the SPUA is in charge of the elaboration and characterization of as-fabricated fuels and then provides input data for the in-pile behavior modeling. Those codes have to be validated, so it requires to achieve characterization on irradiated fuels.
As it is shown in figure 7, irradiation effects induce geometry and microstructure evolutions which have to be quantify. The image analysis procedure presented in this paper could measure, for instance, the evolution of the thickness of each layer, the evolution of kernel diameter. Reorganization of the pyrocarbon structure is an important criteria to be followed before and after irradiation, as well.

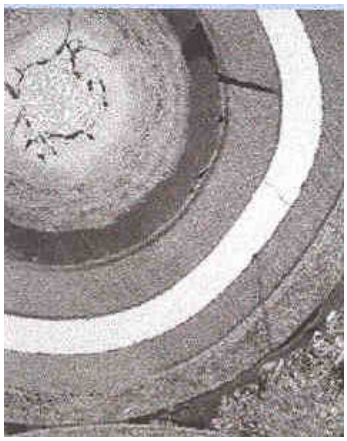

Figure 7 *: irradiated HTR particle*

At this time, a thermal diffusivity measurement device in a hot cell equipped with two remote handling already exists in TUI's facilities (Trans-Uranium Institut). A plan is also under study to install a flash laser equipment in a LECA[1]'s hot cell. Thanks to these devices, the evolution with irradiation of the compact's thermal diffusivity could be evaluated.
Finally, after tests done on active particles with photoreflectance microscope, some adaptations and electronical deports would have to be studied in order to use this equipment in hot cell.

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