



CERN SUMMER STUDENT REPORT

Engineering a novel material

Nanometric titanium carbide particles in a matrix of carbon nanotubes

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INTRODUCTION

The interest of the CERN organization is to study fundamental physics through several experiments at the same time. The LHC enables the study of collisions of proton beams, interpreted by several detectors (known as LHC experiments) like ATLAS, CMS, ALICE, LHCb, TOTEM and so on. Another facility, located at the beginning of the accelerating chain of proton beams, is dedicated to the production and investigation of new isotopes. Its name is ISOLDE, the Isotope Separator On Line Device. Experiments of ISOLDE are focused on studying radioactive nuclei, provided by the interaction between the “low energy” (1.4 GeV) proton beam coming from the Proton Synchrotron Booster (PSB) and a target. This target is a cylinder of specific material, with a small diameter (2 cm) but thick (20 cm). Once the beam reaches the material, protons collide with atoms causing nuclear phenomena like spallation, fission or fragmentation, creating isotopes, which are subjected to diffusion and effusion. Those mechanisms depend on several conditions, among which small particle size and porosity play a key role. In fact, it has been observed that nanometric porous material (a characteristic linked to lower density) present the advantage of having better isotope yields. This is directly linked to the half-life of radioisotopes, since the shorter the half-life the faster the isotopes need to be extracted. If nanometric grains are present and the sample is porous, diffusion is simple and fast so that radionuclides can easily “escape” the target, since atoms have less distance to travel within the material. Once this process has taken place, nuclei can be sent to an ion source and be extracted using an electric potential, creating a beam. However, numerous aspects should be taken in account. If the target is heated to very high temperatures, sintering occurs easily, even if the material is refractory. High temperatures are often needed to obtain faster release times (faster diffusion and effusion). A method has been developed to avoid the material sintering (in the case of powders), but further explanation will be given in this report.

The proton beam can be sent to two target stations: GPS and HRS. The first one, the General Purpose Separator, is composed of one bending magnet only. The second one, the High Resolution Separator, consists of two magnets coupled with an ion-optical system, designed for higher resolving power ^[1]. The isotopes are then delivered to several physics experiments.

In brief, the purpose of this project is to engineer a novel material, a new “target”. Previous experiments have been done with uranium carbide (UC₂), lanthanum carbide (LaC₂) and Calcium Oxide (CaO) ^[2]. Titanium Carbide (TiC) has also been tested in a matrix of carbon black. However, the yield of calcium isotopes was not high enough. The idea is to change the procedure by using Titanium Oxide (TiO₂) in a matrix of Carbon Nanotubes, and finally, thermal treat it to obtain TiC. Ceramics are therefore appreciated because of their refractory properties. This method aroused interest and has been selected as next study, in order to obtain Calcium 35, which half-life is very small - 25.7 milliseconds.

A. GENERAL ASPECTS ABOUT THE PROJECT

1. Description of the approach adopted during the project

It has been decided to follow a similar protocol to that used for previous experiments (see Master thesis from Julien Guillot, “Synthèses et caractérisations de pastilles de carbure de lanthane”^[3] and the work of Alexander Gottberg ^[4], João Pedro Ramos ^{[2][5]} and Wonjoo Hwang). Powder has to be ground and mixed with multi wall carbon nanotubes (MWCNT - *Ref. Nanocyl-3100*), previously suspended in isopropanol (IPA). Afterwards, a drying procedure ensues, where we separate the IPA from the powder. Once this has been carried out, pellets have to be pressed, weighted, measured and characterized in order to analyse the microstructure of the solid material and to determine their density.

Sintering often occurs with ceramics and can involve partial fusion of the material, leading to an increase of compactness and thereby a decrease of porosity. It is a process used to enhance properties such as strength, translucency, thermal and electrical conductivity^[6]. Several steps lead to formation of big grains, this phenomenon being controlled by atomic diffusion and thereby strongly dependent on the evolution of temperature. However, in this case, it is considered as harmful for the target experiment and has to be bypassed, hence the use of MWCNT.

CNT (and MWCNT) are allotropes of carbon with a cylindrical nanostructure and can have an incredible length-to-diameter ratio (in our case 20 nm diameter and few microns in length). Their melting point is extremely high (about 3500°C), making them favourite candidates for the “target” experiment. ^[7] Moreover, they avoid contact between the TiO₂ particles, separating them from each other, avoiding in this way that they sinter together. The material will then be submitted to carbothermal reduction to obtain nanometric TiC particles suspended in the nanotubes. Therefore, as the temperature of the target has to be as high as possible to provide better diffusion mechanisms, MWCNT enable the operator to easily reach very high temperatures without risking to sinter the material.

2. Tools and methods available / detailed protocol.

First of all, TiO₂ powder has to be ground. Two products are at our disposal named after the company producing them: “Alfa Aesar” (*Ref. 39953*) and “Sigma Aldrich” (*Ref. 634662-100G*), both nanosized. The first powder contains particles smaller than 35 nm in average, and the second particles with less than 100 nm of size. Once the TiO₂ product, isopropanol and tungsten carbide grinding balls (with proportions estimated in previous studies ^[3]) have been

introduced in the planetary mill, the operator has to select parameters like revolution per minute, grinding and pause time, as well as repetition of rotations. One will find more information about the influence of each parameter on particle size distribution further in the report (**Part B**). During the milling process, the mixture of CNT and IPA was prepared in a 1L beaker subjected to agitation and Ultrasound for one hour. The final purpose is to mix everything together, CNT, IPA and TiO₂ suspension. Afterwards, the mixture is dried with a technique inspired by the principle of a rotary evaporator. Thus, we obtain a bulk of material composed of TiO₂ powder and tangled Carbon Nanotubes. Then the obtained product is deagglomerated into fine powder thanks to an agate mortar, to prepare for the next step: the pressing of pellets. Two tons for ~30 s are applied on 300 mg of powder, forming cylindrical tablets. Afterwards, those pellets are carburised in a vacuum oven, reaching very high temperatures to provide diffusion of carbon atoms, which react with Titanium Oxide. The characterization can be done with the help of X-Ray Diffraction (XRD) for phase identification and Scanning Electron Microscopy (SEM) for microstructure morphology. On the other hand, mesoporosity can be calculated using nitrogen adsorption, based on the Brunauer-Emmet-Teller theory (BET). Several information will be provided in **Part C**.

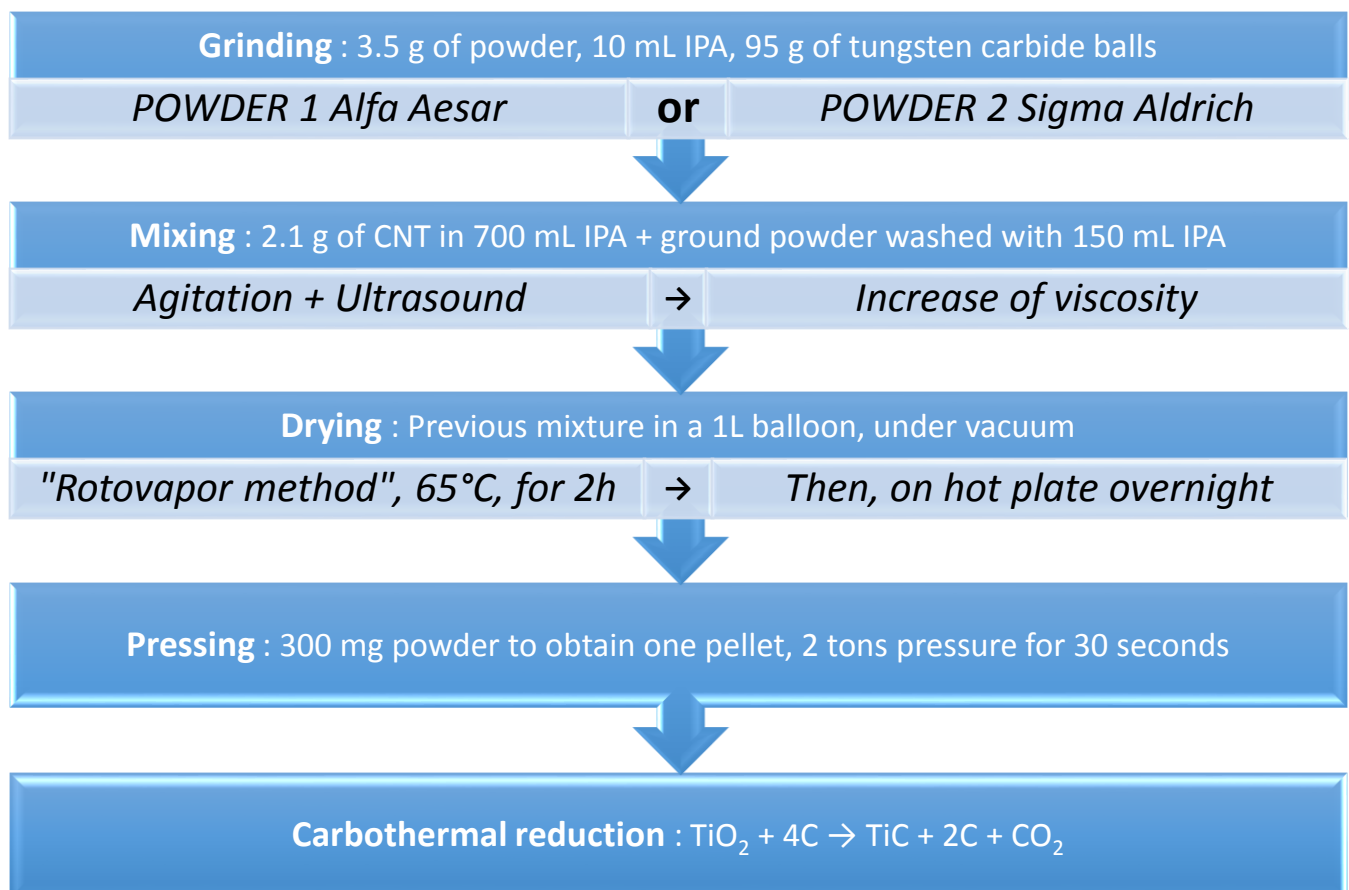


Figure 1: Process diagram of the employed method

B. PRELIMINARY EXPERIMENTS: OPTIMISATION OF THE MATERIAL SYNTHESIS

1. Influence of grinding time on particle size distribution

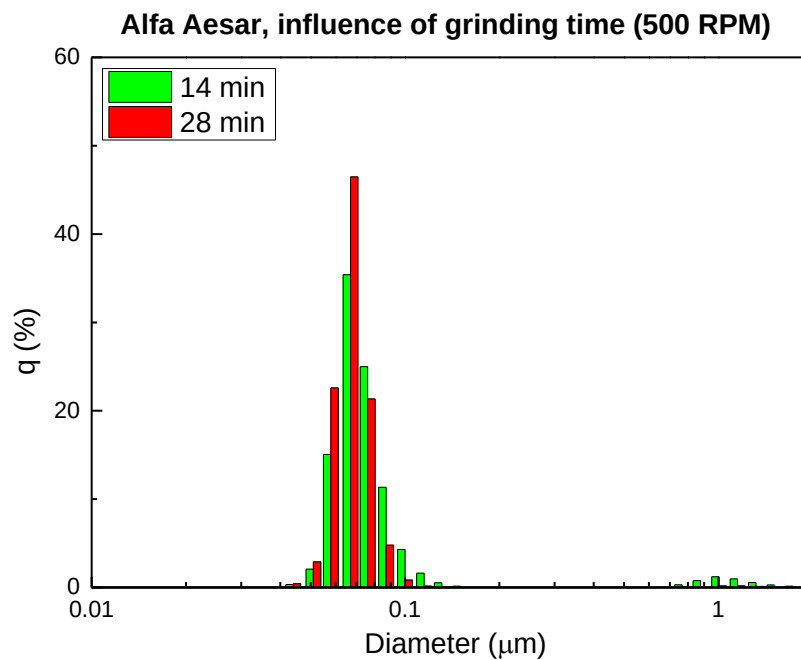


Figure 2: Influence of grinding time on the particle size distribution of the **Alfa Aesar** powder (1)

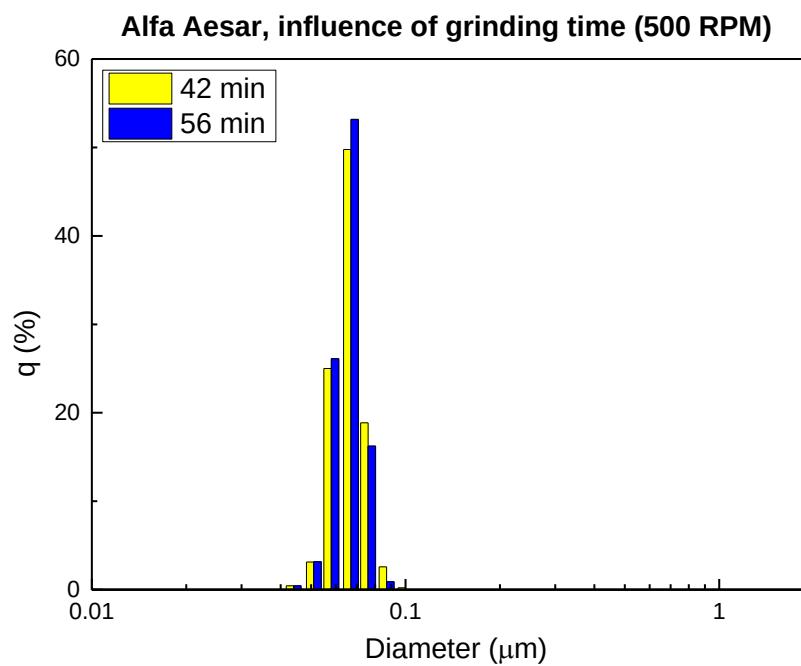


Figure 3: Influence of grinding time on the particle size distribution of the **Alfa Aesar** powder (2)

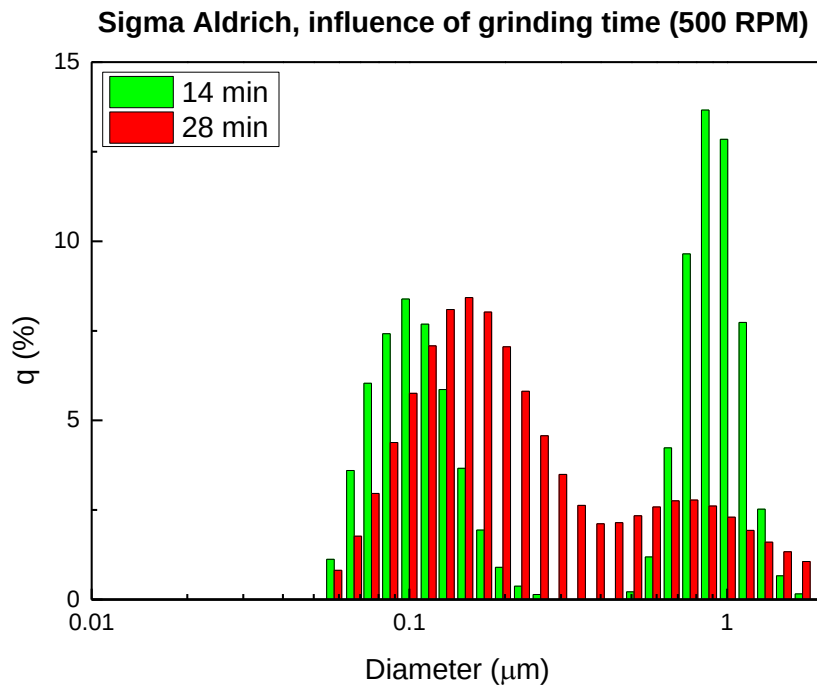


Figure 4: Influence of grinding time on the particle size distribution of the **Sigma Aldrich** powder (1)

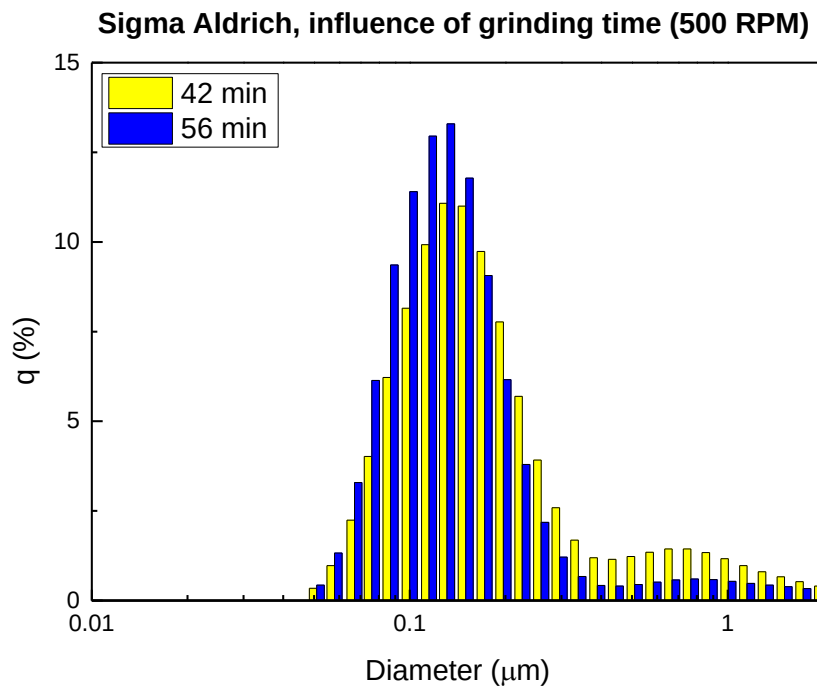


Figure 5: Influence of grinding time on the particle size distribution of the **Sigma Aldrich** powder (2)

The previous four graphs show us the effect of grinding time on the particle size distribution of each powder. Each experiment consists of two steps: grinding and ultrasonic dispersing before measuring. One can observe a significant difference between “Alfa Aesar” and “Sigma Aldrich” (Figures 2 to 7). In fact, on Figures 2 and 3, the “Alfa Aesar” powder presents a narrow peak on the left of the diagram, showing that most of the particles have a size of 70 to 80 nm.

There is no real contrast between short and long grinding times, the shape of the graph almost remaining the same after 14 and 56 minutes. The “Sigma Aldrich” powder, on the contrary, displays a noteworthy shifting from right to left, to smaller sizes, on Figures 4 and 5. Time influence is easily observable by reviewing the minimum and maximum grinding times, on Figures 3 and 5. At the beginning of the experiment (green columns on Figure 4), the amount of agglomerates and bigger particles is leading, as seen on the logarithmic scale on abscissa, around 1 μm . After 28 minutes, those agglomerates are destroyed by the milling, hence the shifting phenomenon and the increase of the column size around 0.2 μm . Finally, the operator may be able to deagglomerate nearly all after one hour of grinding (blue columns on Figure 5).

2. Effect of the “Revolutions Per Minute” (RPM) value on the powder dimensions

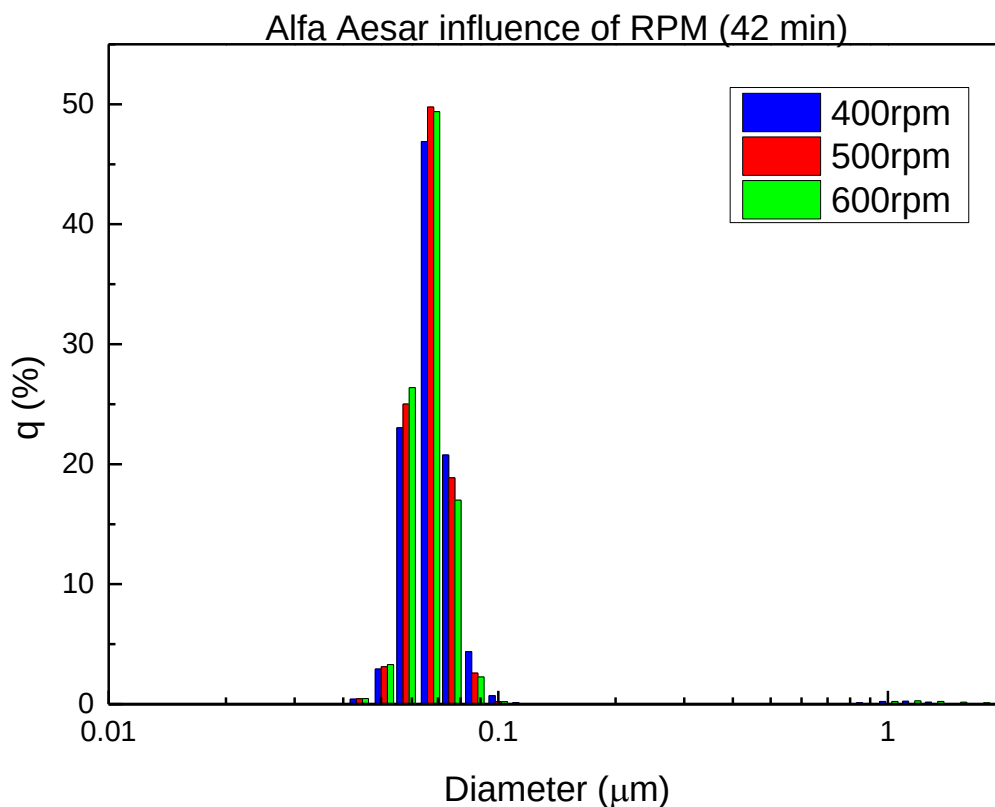


Figure 6: Impact of the RPM value on the size distribution of the **Alfa Aesar** powder

The next step was to study how RPM affects the size distribution. According to the graph on Figure 6, hereinabove, there is no influence on the particle size of “Alfa Aesar”, whether the experimenter choose 400, 500 or 600 RPM. For optimisation reasons, the 500 RPM value has been retained for the project.

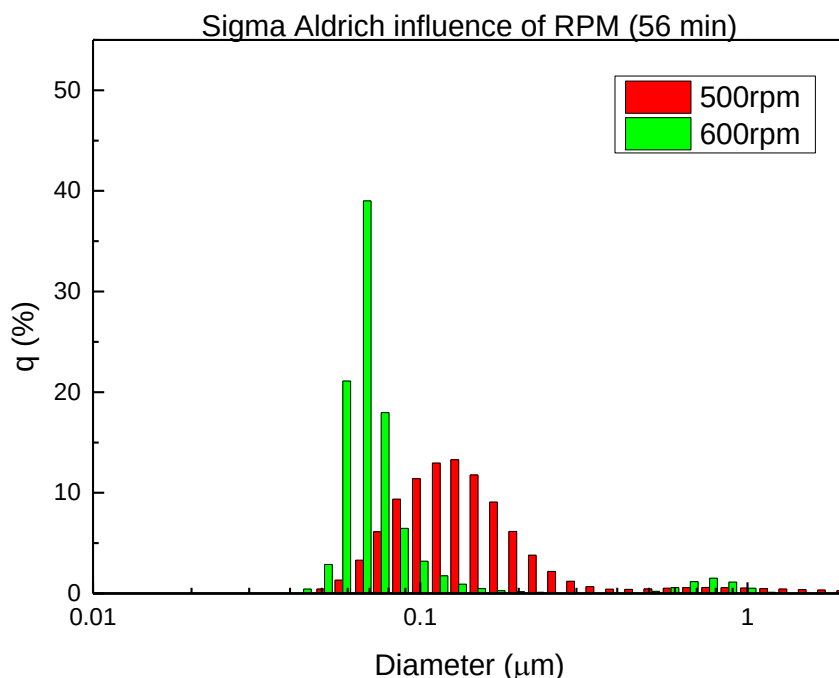


Figure 7: Impact of the RPM value on the size distribution of the **Sigma Aldrich** powder

For “Sigma Aldrich”, on the other hand, there is a distinct shifting by changing the RPM value. As observed on Figure 7, above, 600 RPM is more efficient than 500 RPM.

Finally, following settings have been retained: the “Alfa Aesar” powder has to be ground for 42 minutes, at 500 RPM. This involves defining the parameters of the planetary mill with 5 repetitions of 7 minutes, including 1 minute pause between each rotation direction. For “Sigma Aldrich”, we keep about the same process, by adding extra 14 minutes and by grinding the powder at 600 RPM. The initial particle distributions of both powders with and without ultrasound can be found on Figures A1 and A2 in the annexe. The break between each functioning is made because of the fast rise of temperature inside the jar to allow for cooling (each tungsten carbide ball undergoes about 30 G, which is a lot of energy converted in heat).

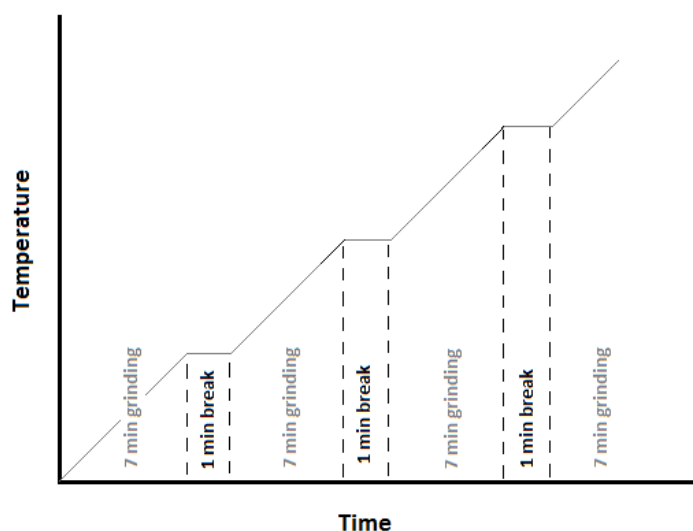
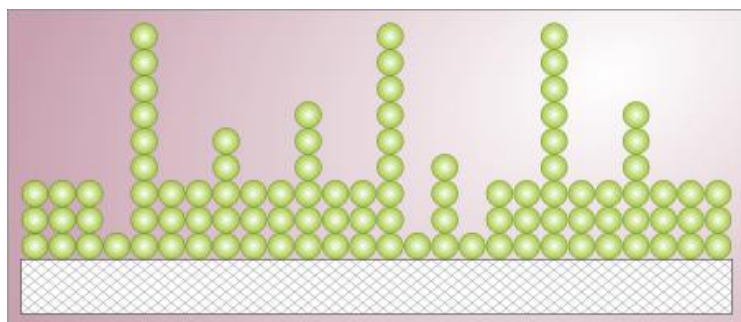


Figure 8: Temperature cycle inside the jar: Breaks done to avoid increase of temperature

C. EXPERIMENTAL RESULTS

1. Study of porosity: BET method

To estimate the porosity of our final product, we call in the principle of adsorption. Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid or dissolved solid to a surface. Desorption is the reverse process of it [8]. Both enable the outline of isotherms, which make possible the estimation of the specific surface area thanks to the Brunauer-Emmet-Teller (BET) equation. In our case, nitrogen (N_2) is used as adsorbate. Knowing the surface of a N_2



molecule and using the desorption curve, the software gave us the specific surface area of both powders, took as raw product.

Figure 9: BET Multilayer adsorption model: random distribution of sites [8]

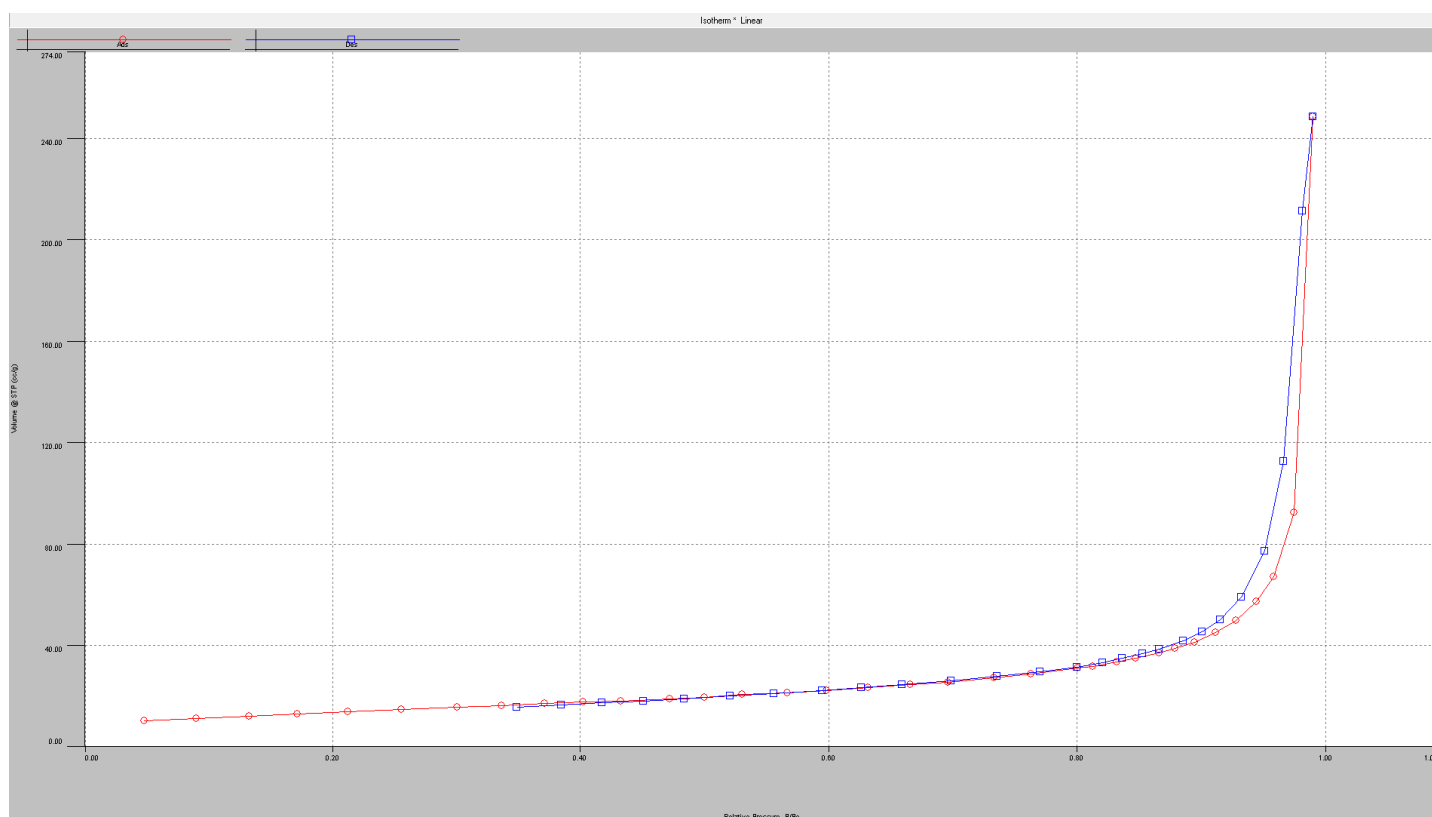


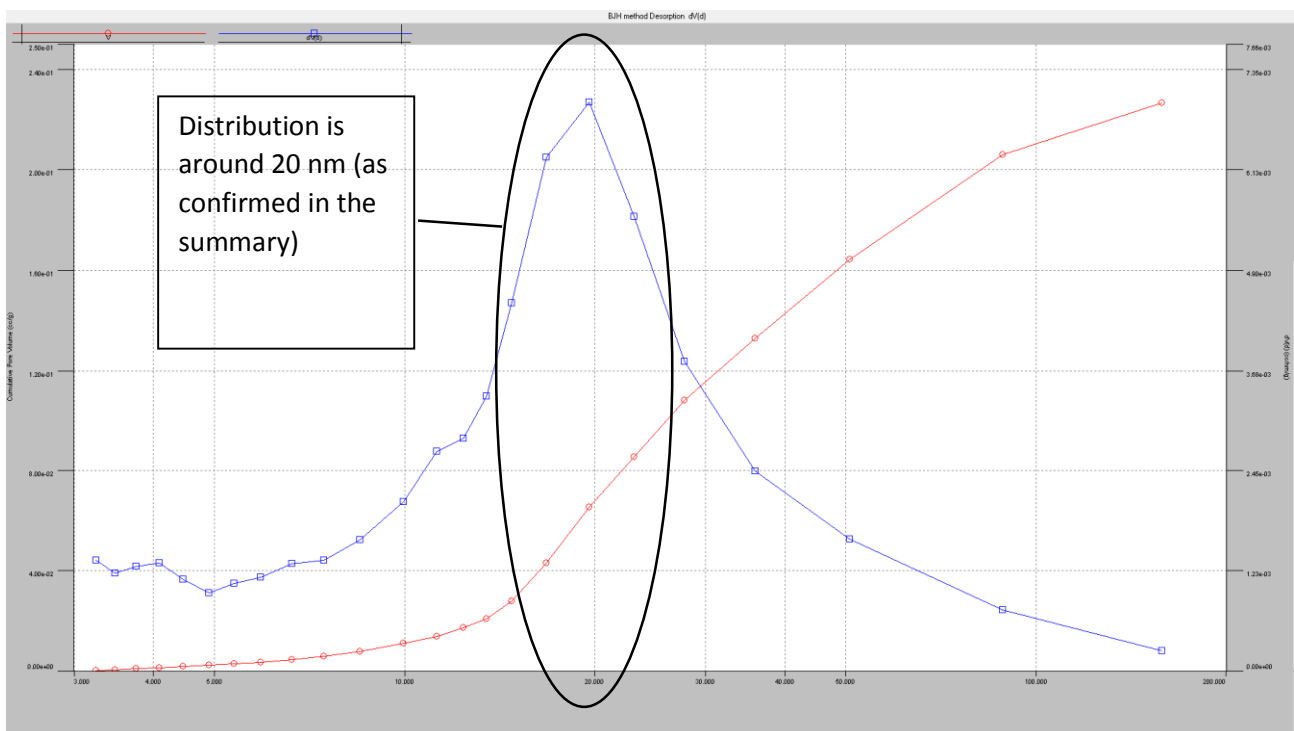
Figure 10: Adsorption/Desorption isotherms for Alfa Aesar (raw product)

On the graph of the Figure 10, we can observe a typical hysteresis loop, showing that both adsorption (red) and desorption (blue) curves do not coincide. In our case, the phenomenon of adsorption is more specifically called physisorption, usually a reversible process, whereby molecules are kept on the surface by the weak Van der Waals forces. However, in mesoporous materials, with pores with diameters between 2 and 50 nm, this process tells about the pore sizes. Indeed, it is linked to what one call capillary condensation, a phenomenon by which pore spaces become filled with condensed liquid from the vapour phase, hence this characteristic curve shape. [9]

The BET equation states that: $\frac{p}{V(p_0-p)} = \frac{1}{VmC} + \frac{C-1}{VmC} \frac{p}{p_0}$

By plotting $\frac{p}{V(p_0-p)}$ in function of $\frac{p}{p_0}$, it gives us following parameters: C constant, slope, intercept and surface area. The “Alfa Aesar” powder being composed of smaller particles than “Sigma Aldrich”, its surface area is greater (48.055 m²/g against 37.484 m²/g). The surface area is calculated by using only the left part of the isotherm, corresponding to the adsorption of the first layer of N₂ (monolayer).

Finally, information about pore size is given by the Barrett-Joyner-Halenda (BJH) analysis. The material is composed of mesopores as shown on the pictures below, knowing that a mesopore has a size between 2 and 50 nm.



BJH desorption summary

Surface Area = 34.388 m²/g
Pore Volume = 0.227 cc/g
Pore Diameter D_v(d) = 19.620 nm

Figure 11: BJH Desorption curve and summary for Sigma Aldrich

2. Mass loss and shrinkage estimation

After carbothermal reduction, size and weight of the samples changed drastically. It appears that sintering slightly occurs, reducing the dimensions of the pellets, even though the material contains carbon nanotubes. This is a proof that this phenomenon can only be hindered, but not prevented.

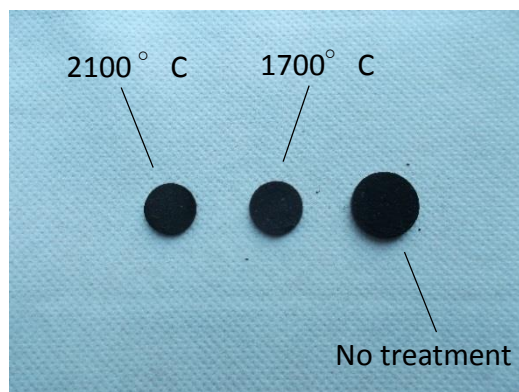


Table 1: Calculation of density before carburisation, first set: **Alfa Aesar** (pellet **A**, **B** and **C**) / **Sigma Aldrich** (pellet **D**, **E** and **F**)

Pellet	Weight (g)	Diameter (mm)	Thickness (mm)	Volume (cm ³)	Density (g.cm ⁻³)
A	0.2912	15.48	2.14	0.402	0.724
B	0.2879	15.55	2.27	0.431	0.668
C	0.2956	15.51	2.35	0.444	0.666
D	0.2989	15.50	2.31	0.436	0.686
E	0.2995	15.57	2.32	0.442	0.678
F	0.2953	15.51	2.33	0.440	0.671

Table 2: Calculation of density before carburisation, second set: **Alfa Aesar** (pellet **G**, **H** and **I**) / **Sigma Aldrich** (pellet **J**, **K** and **L**)

Pellet	Weight (g)	Diameter (mm)	Thickness (mm)	Volume (cm ³)	Density (g.cm ⁻³)
G	0.2962	15.45	2.17	0.407	0.728
H	0.2960	15.48	2.19	0.412	0.718
I	0.2977	15.49	2.20	0.415	0.717
J	0.2894	15.50	2.23	0.421	0.687
K	0.3001	15.54	2.31	0.438	0.685
L	0.2979	15.55	2.22	0.422	0.705

Both table 1 and 2 above show measurements about size and weight before the heat treatment. In average, these pellets have a diameter of 15.5 mm, a thickness of 2.25 mm and a weight of 295 mg. Density is around 0.7 g.cm⁻³.

Two pellets among three have been thermo-treated in a vacuum oven, reaching first the temperature of 2100 °C (for the first set). After plotting graphs displaying pressure versus temperature, it seemed like the carburising reaction occurs between 1300 °C and 1500 °C, and thereby, further treatment have been operated until 1700 °C (second set).

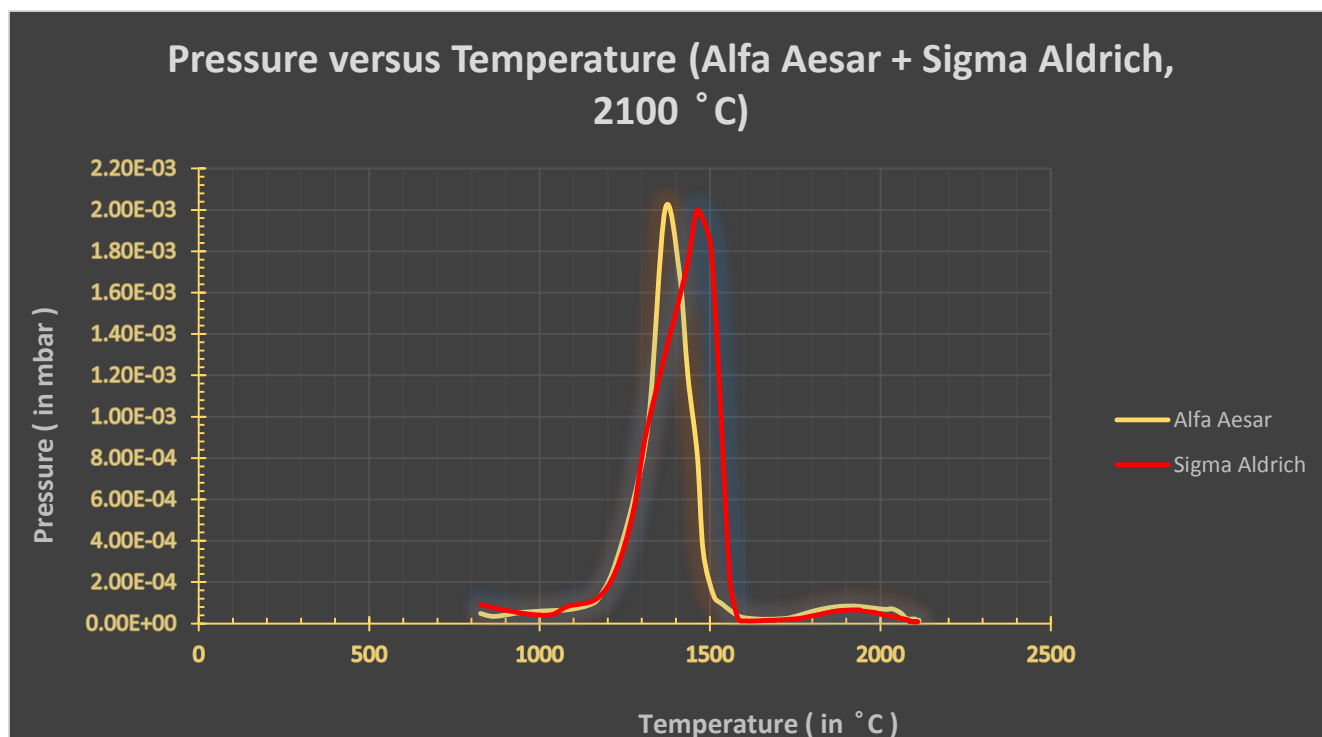


Figure 12: Graph displaying pressure versus temperature for both powders, after carbothermal treatment

Several peaks have been observed, by plotting the evolution of pressure over time. The first small peak, appearing around the 21st minute of the experiment (Annexe Figure A3), corresponds to the evaporation of remaining Isopropyl Alcohol and water. The second one, the main peak, appears around 30 minutes (about 1400 °C on the graph of Figure 12) and matches to the carburisation, with an increase of pressure from 3.10^{-5} to 2.10^{-3} mbar.

Table 3: Calculation of density after carburisation at 2100 °C, first set: **Alfa Aesar** (pellet **A** and **B**) / **Sigma Aldrich** (pellet **D** and **E**)

Pellet	Weight (g)	Diameter (mm)	Thickness (mm)	Volume (cm ³)	Density (g.cm ⁻³)
A	0.1654	12.19	1.68	0.196	0.844
B	0.1644	12.24	1.70	0.200	0.822
D	0.1655	12.87	1.91	0.248	0.667
E	0.1657	12.94	1.94	0.255	0.650

Table 4: Calculation of density after carburisation at 1700 °C, second set: **Alfa Aesar** (pellet **G** and **H**) / **Sigma Aldrich** (pellet **J** and **K**)

Pellet	Weight (g)	Diameter (mm)	Thickness (mm)	Volume (cm ³)	Density (g.cm ⁻³)
G	0.1670	12.97	1.90	0.251	0.665
H	0.1678	12.67	1.91	0.241	0.696
J	0.1616	13.10	1.82	0.245	0.660
K	0.1679	13.18	1.92	0.262	0.641

The tables 3 and 4 display the dimensions of the pellets after heat treatment, as well as their weight. This data enables the calculation of mass loss and shrinkage, by using the following formula,

$$\text{loss in \%} = \frac{\Delta x}{x_i} * 100 = \frac{x_i - x_f}{x_i} * 100$$

where x_i is the parameter before carburising and x_f the parameter after heat treatment.

Therefore, by comparing both powders (Alfa Aesar and Sigma Aldrich in table 5), we notice a slight difference in the shrinkage value (~ 2 %, between the 1700°C set), but mass loss remains the same. Then, comparing same powders but at different treatment temperatures leads to the following conclusion: the material is quite stable (no significant difference in mass loss and especially shrinkage).

These results are displayed in the table below.

Table 5: Calculation of mass loss and shrinkage at 1700 °C and 2100 °C: **Alfa Aesar** (pellet **A**, **B**, **G** and **H**) / **Sigma Aldrich** (pellet **D**, **E**, **J** and **K**)

Pellets	1700 °C		2100 °C	
	Mass loss (%)	Shrinkage $\Delta D/D$ (%)	Mass loss (%)	Shrinkage $\Delta D/D$ (%)
A	/	/	43	21
B	/	/	43	21
G	44	16	/	/
H	43	18	/	/
D	/	/	45	17
E	/	/	45	17
J	44	15	/	/
K	44	15	/	/

CONCLUSION and OUTLINE

To summarize, this study led to very positive results. The optimisation of the material synthesis showed which time and RPM values have to be chosen for the grinding step. In fact, as the powder was highly agglomerated, simple ultrasound was not enough to separate the particles from each other, and a planetary mill was required to obtain the adequate particle size distribution (below 100 nm).

BET outcomes were complementary to particle size analysis, by indicating the porosity of the material. This technique has been used on the raw product only, but further experiments should be done on the carburised samples as well.

Shrinkage of the pellets after carbothermal reduction is an indicator of sintering, which confirms that MWCNT cannot fully prevent it. However, as carburisation has been done with two different temperatures and since weigh losses are not significantly different, the material is considered as very stable.

Nevertheless, the study has to be continued by reviewing microstructure and porosity of the target material with help of Scanning Electron Microscopy. Additionally, phase analysis will be done using X-Ray Diffraction.

Finally, if these results are significant enough, the target material can be approved and tested at the ISOLDE facility, hoping to produce isotopes with a favourable yield.

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- “Synthèses et caractérisations de pastilles de carbure de lanthane”, Julien GUILLOT, Rapport de stage, CERN, 2014 [3]
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- “Hysteresis Phenomena in Mesoporous Materials”, Sergej Naumov, available on http://www.uni-leipzig.de/~gfp/sites/default/files/27-dr._sergej_naumov/dissertation.pdf [9]

USEFUL INFORMATION

- “Measurement of Surface Area by gas sorption” – Explanation in the video on http://www.quantachrome.com/technologies/surface_area.html
- “Role of some technological parameters during carburizing titanium dioxide”, available on <http://www.sciencedirect.com/science/article/pii/S0955221999000746>
- Surface Modification Techniques for Biomedical Grade of Titanium Alloys: Oxidation, Carburization and Ion Implantation Processes, available on <http://www.intechopen.com/books/titanium-alloys-towards-achieving-enhanced-properties-for-diversified-applications/surface-modification-techniques-for-biomedical-grade-of-titanium-alloys-oxidation-carburization-and->

ANNEXE

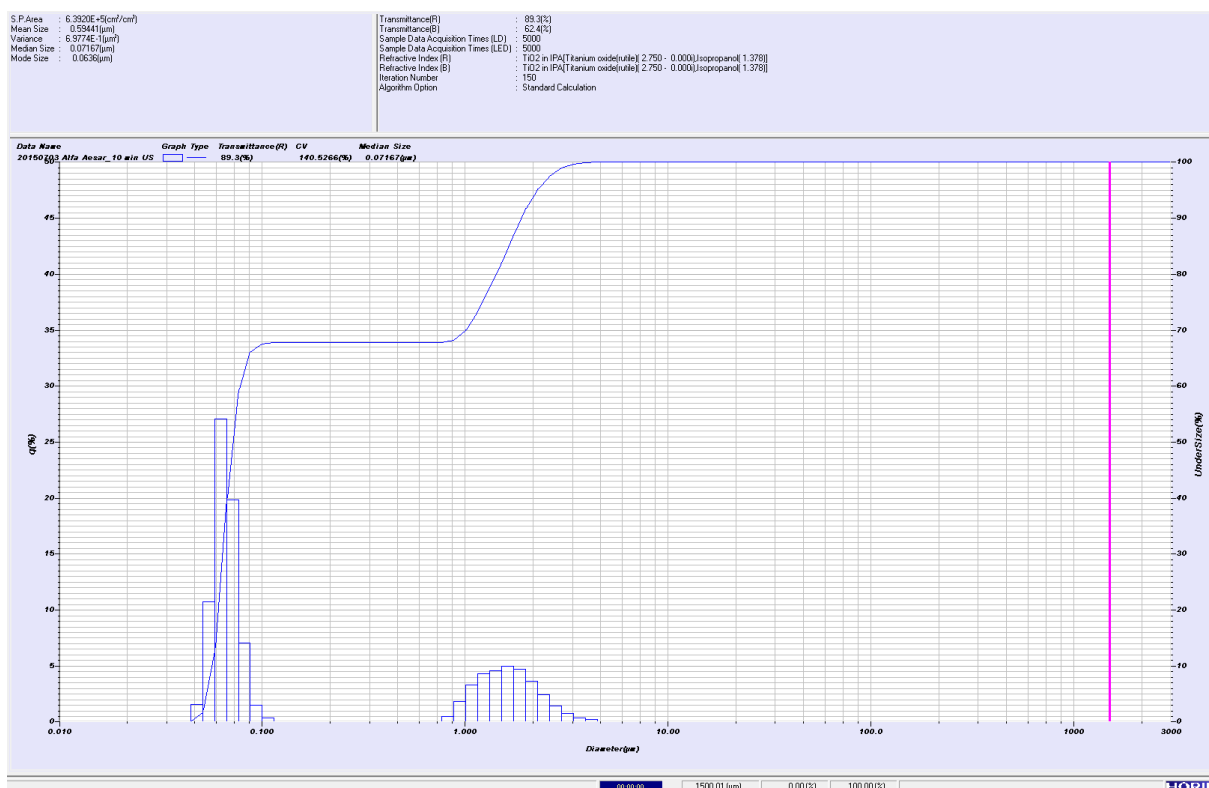
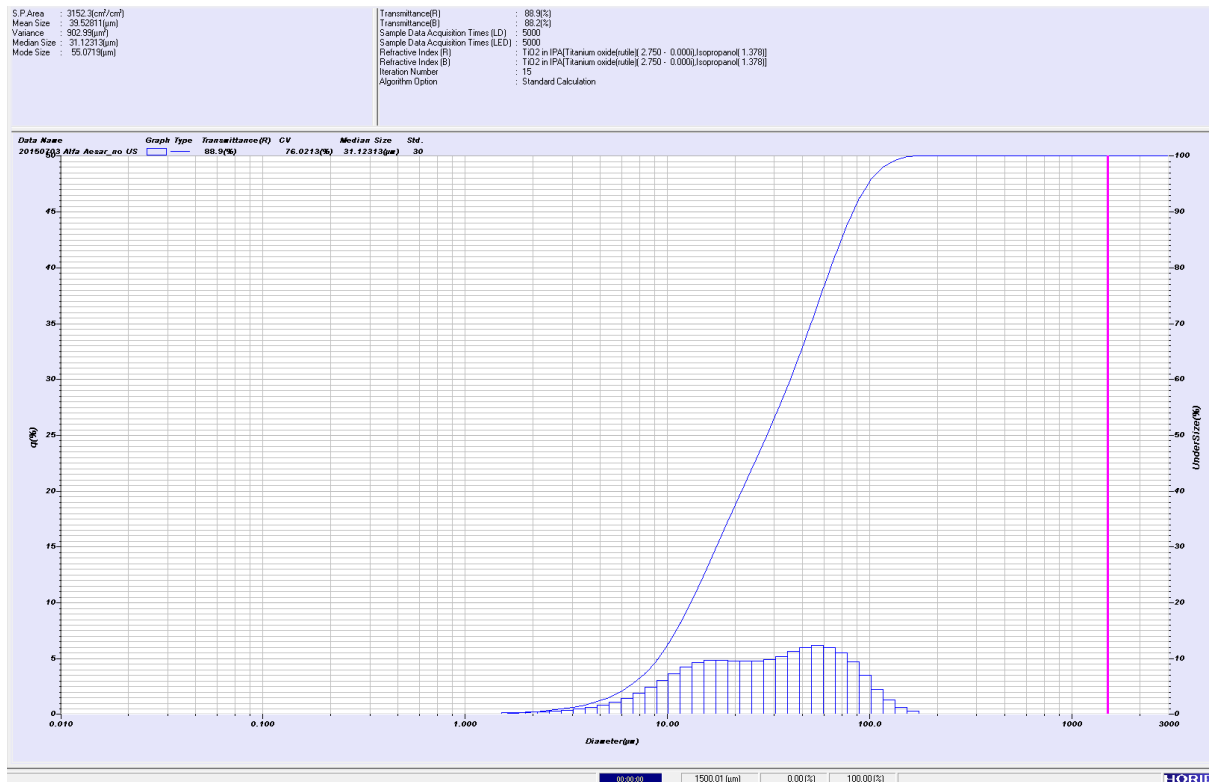


Figure A1: Particle size distribution of the “Alfa Aesar” powder before (above) and after ultrasound (below).

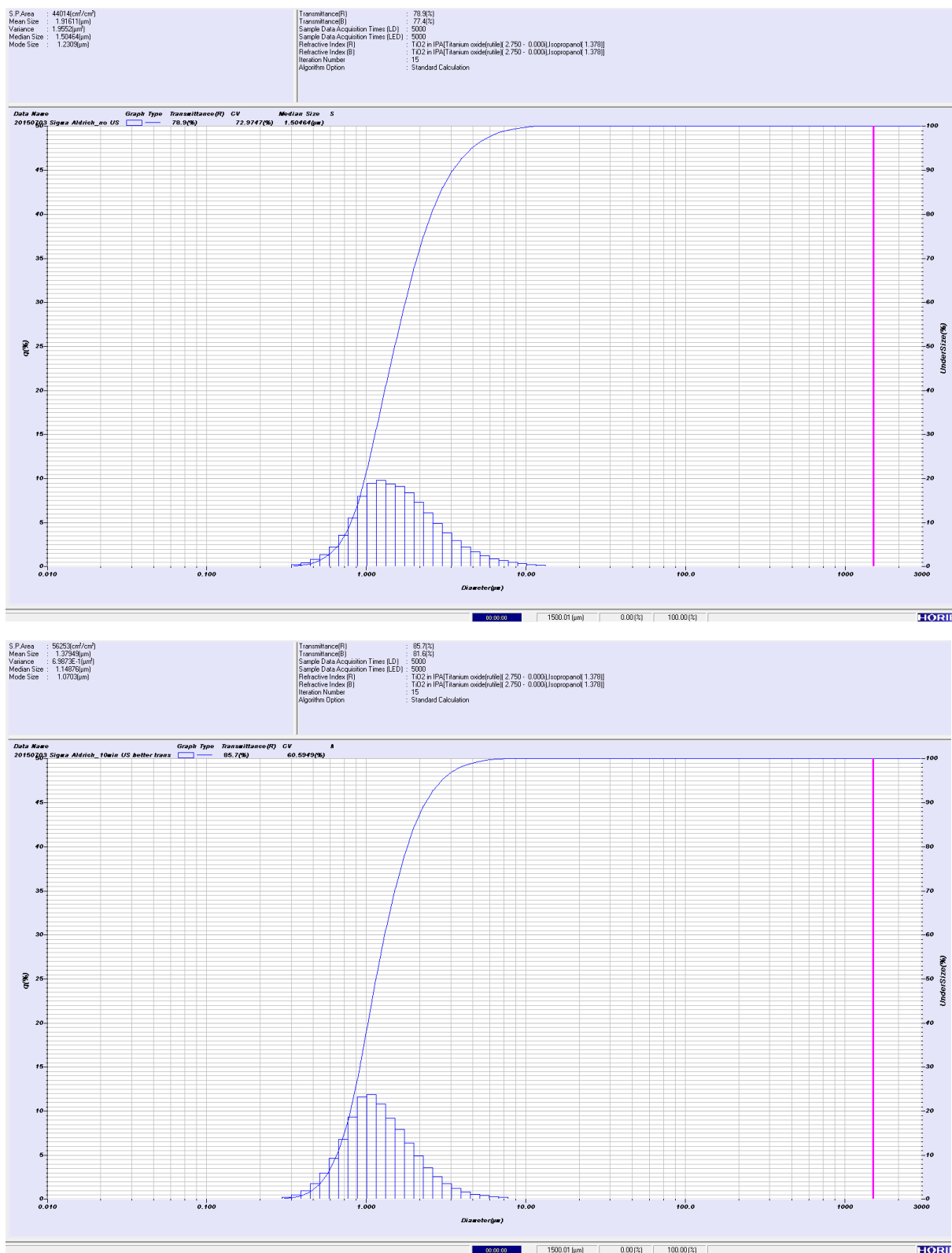


Figure A2: Particle size distribution of the “Sigma Aldrich” powder before (above) and after ultrasound (below).

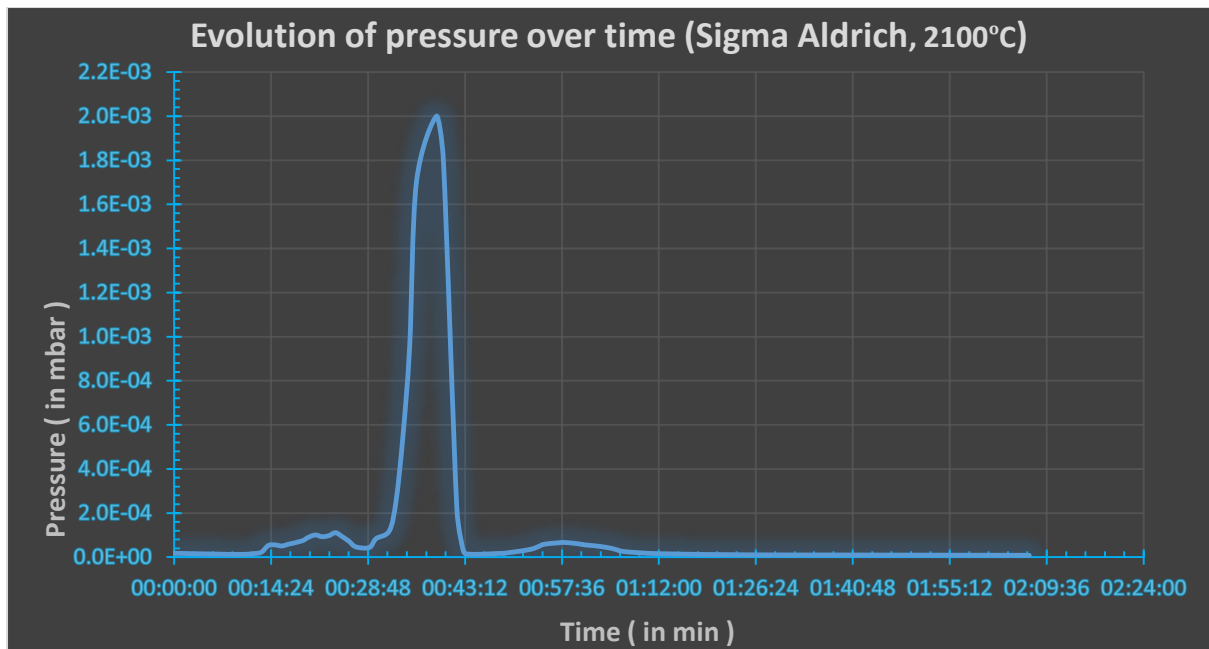


Figure A3: Pressure evolution over time during carburization. The first peak is below 800°C while the second peak, corresponding to the carburization, is between 1300 and 1700°C.