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# Influence of the sintering atmosphere on dense Uranium mono-carbide properties

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## Abstract

Mixed (U, Pu) carbides are potential candidate fuels for future IV<sup>th</sup> generation reactor systems because of their high fissile atom density and their excellent thermal properties. They could contribute to an economical, more compact and efficient core design. Much less studied than oxides, a reassessment of their properties from more recent microanalysis techniques developed for the characterization of uranium oxides could draw benefit. Investigations will focus on UC considered to be a valid surrogate material for R&D studies on (U,Pu)C fuels. UC possesses a similar NaCl type crystal structure and allows larger possibilities for characterization with available techniques. UC is also thought to be a more simple system than uranium-plutonium mixed carbides.

The object of this paper is the study of the influence of manufacturing parameters upon the microstructural properties of dense mono-carbides. The narrow range of composition over which the material is stable and its general chemical instability are the cause of many manufacturing difficulties. The carbo-thermic reaction using a mixture of UO<sub>2</sub> and carbon was used as the easiest way to synthesize the carbide powder. Because carbides will slowly oxidize in air, all fabrication stages and equipment required for sample preparation are handled in glove boxes in an argon atmosphere with particularly low oxygen content. Optimized processing conditions have been investigated in order to obtain a high density, single phase material after sintering. The influence of four sintering atmospheres has been investigated such as low vacuum, pure argon, argon/hydrogen and argon/hydrogen/methane. Their influences on sample chemical and physical characteristics are presented.

## 1 Introduction

Mixed Uranium Plutonium carbides are possible fuel candidates for generation IV nuclear reactors because of their remarkable properties. Compared to oxide fuels, carbides have a higher actinide density and greater thermal conductivity [1, 2]. During in-pile operation, these fuels have a potentially enhanced breeding ratio in Fast Neutron Reactors (FNR) and temperature gradients across the fuel pellet radius lower than for oxide fuels. Their high melting point combined with their high thermal conductivity [3], depending on reactor core design, lead to a lower operating temperature for equivalent linear heat rates hence a greater margin to fusion.

Only few in pile experimentations have been carried out so far in France but carbide fuels have shown larger swelling coefficients [4] after irradiation than mixed oxides. In order to generate additional knowledge on carbide fuel behaviour, complementary characterizations are needed particularly in the field of fission gas behaviour often thought to be one of the main causes of swelling.

Because plutonium compounds require draconian handling restrictions and can only be characterized on a limited number of shielded instruments, we have chosen to begin these studies with UC mono-carbides as surrogate for mixed carbides. Uranium mono-carbide has the same crystallographic rock salt structure as NaCl also common to some mixed carbide phases.

The requirements for studying UC samples so that intrinsic properties may readily be characterized are that:

- they are made up of a single phase,
- they exhibit a high level of purity, (especially with low oxygen and nitrogen content),
- their apparent density is in excess of 95 % theoretical density,
- they exhibit reasonably large grain size (more than 10  $\mu\text{m}$ ) so that the microstructure may be considered stable.

## 2 Uranium carbide Sample preparation

### 2.1 Specificities of uranium mono-carbide preparation

Uranium carbide shows a metallic type bonding and has specific properties and chemical behaviour.

In powder form in air, uranium carbide has a remarkable pyrophoric behaviour [5]. A small mechanical load can provide enough energy to start a high speed oxidation process. At room temperature, in air, dense uranium carbide reacts slowly with oxygen and nitrogen to give oxy-carbide or carbo nitride corrosion layers. Moisture is also an efficient corrosion promoter [6]. This material is very sensitive to corrosion as a result of solid-gas exchanges, which justifies taking strict precautions in relation to sample preparation and storage. The ideal conditions for handling this material consists of a purified argon atmosphere [4] with moisture and oxygen levels lower than 25 ppm.

However, it should be noted that for many characterisations conducted on large scientific instruments, the sample and the sample holder have to be assembled in air because of the absence of controlled atmosphere glove boxes. It implies that oxygen contamination is likely to occur and may lead to irreversible changes in the sample. This requires that a strategy be devised for sample manufacturing preparation and storage. A sufficiently large number of samples of reproducible characteristics need to be prepared to insure consistency in results and provide for a sufficiently large number of techniques being implemented.

### 2.2 Uranium carbon metastable phase diagram

The U-C diagram, figure 1, [7] shows mono, di and sesqui-uranium carbide phases.

The region in which the mono carbide phase is stable is very narrow at low temperature, which means that a small deviation from a stoichiometric composition will result in material containing a secondary either metallic or di-carbide phase. For process control, this implies that stoichiometry control will be one of the key parameters for manufacturing. Also the existence of a non-stoichiometric phase suggests that in the stoichiometric region, point defect concentrations hence properties will vary substantially [3, 8].

In practice, Uranium sesqui-carbide is difficult to synthesize [2] and is never observed when standard ceramic manufacturing processes are used [9] such as the route described in figure 1 or by powder sintering or using an arc melting furnace [10, 11]. Uranium di carbides on the other hand even if they are thermodynamically metastable at room temperature, are commonly observed instead. Di-carbide dissociates into sesqui-carbide with a limited kinetic.

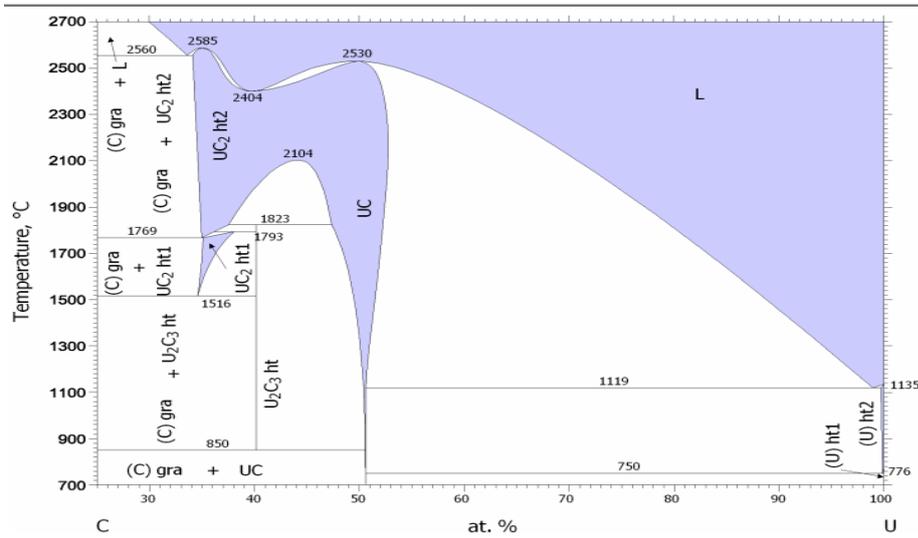


Figure 1: Binary U-C phase diagram [7, 12]

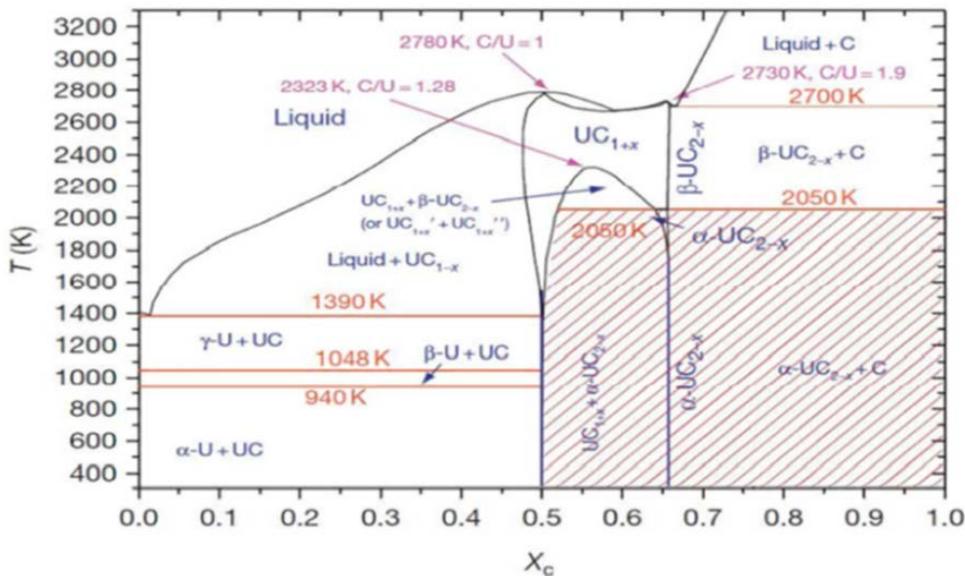


Figure 2: Metastable Phase diagram [13].

A meta-stable diagram (figure 2) proposed by Laugier [13], gives more practical information in relation to phases actually encountered when using typical ceramic processing techniques. This representation illustrates in particular the narrow UC single phase domain and the important second phase domains.

Figure 3 gives examples of sample microstructures obtained with different U/C ratios close to a stoichiometric composition.

When the molar U/C ratio is greater than unity, a metallic uranium phase may be present at the grain boundaries providing a liquid phase during sintering and enhancing both sintering and grain growth. When the U/C ratio is less than unity, a di-carbide second phase will be present in the sample giving the so called typical Widmanstätten pattern [14], easy to recognize on optical micrographs.

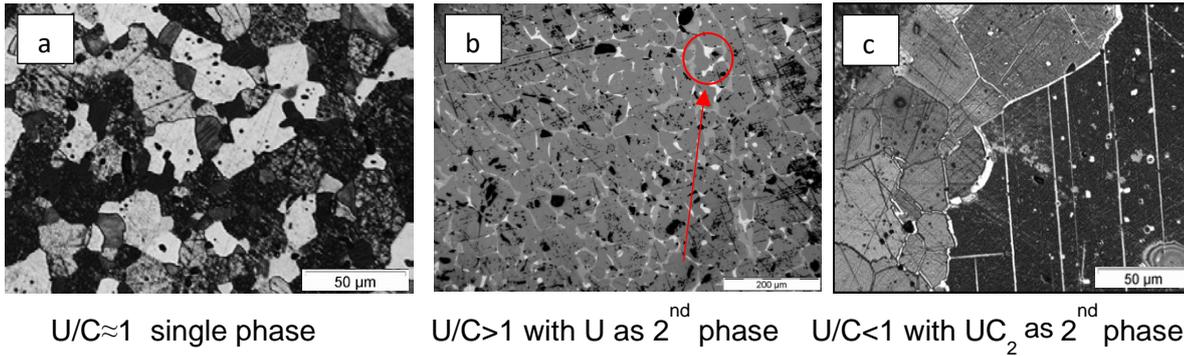


Figure 3: View of a typical sample optical microstructures depending on the U/C ratio a) UC single phase, b) UC with U second phase at the grain boundaries, c)  $UC_2$  phase.

Figure 3-a gives a common picture of UC single phase material. Grains can be easily identified because surface oxidation depends on crystal orientation which results in different level of grey. In picture 3- b metal uranium can be seen at grain boundaries in bright. Picture 3-c shows the typical Widmanstätten pattern corresponding to a  $UC_2$  region.

Great care and effort have gone into material processing in order to insure that the end product was essentially made up of a single carbide phase. One necessary condition for this is to avoid any gas pollution of the argon atmosphere. A specific setup of two glove boxes (figure 4) has been used for uranium carbide manufacturing and sample preparation. All the necessary equipment for ceramic manufacturing and processing was made available within the gloveboxes in an oxygen free environment.

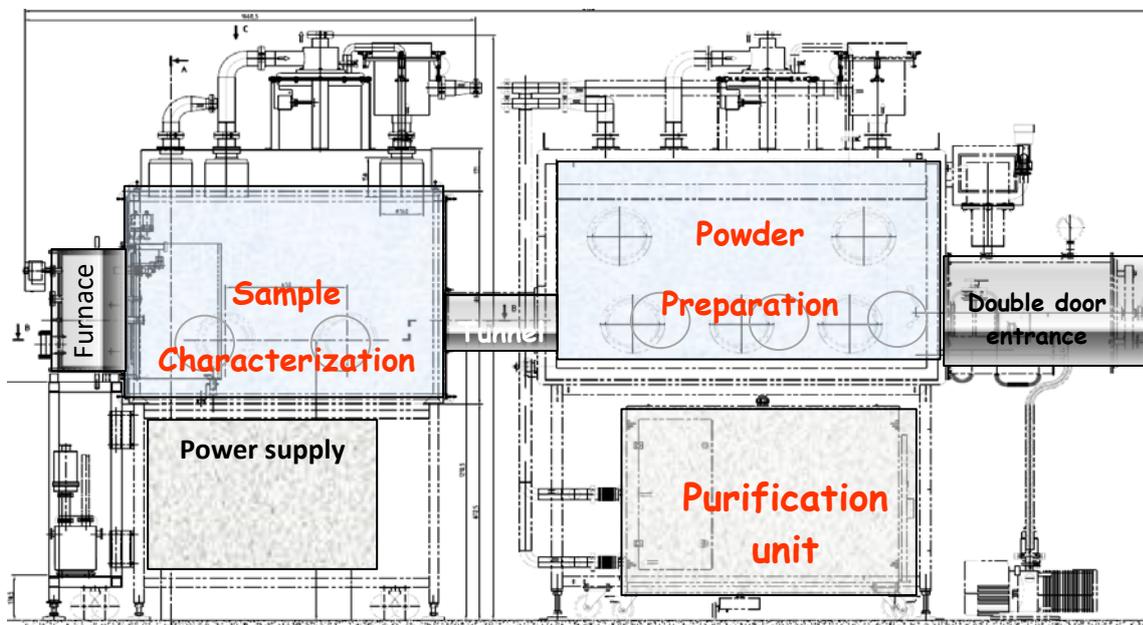


Figure 4: Glove boxes for uranium carbide preparation

The glove box's atmosphere is continuously controlled, renewed and purified. The purification unit is supplied by Jacomex®- France and the monitoring of the atmosphere indicates  $O_2$  and water contents below 10 ppm. A metallic tungsten furnace (custom made by SPG – France for glove box adaptation) is connected to one of the

glove boxes. The maximum achievable furnace temperature is about 1900°C and different atmospheres such as vacuum, neutral or reducing gas mixtures are available.

The general process is described in figure 5. The process steps are divided in two stages: carbide synthesis and carbide densification. The synthesis route chosen is the well-known carbo-reduction [15] from uranium dioxide by carbon addition.



Equation 1 gives an expression of the global synthesis reaction. An adjusted carbon addition is one important factor for final U/C ratio control.

Uranium dioxide slowly becomes hyper-stoichiometric during its storage in air, giving UO<sub>x</sub> (with x>2) at the surface. The phenomenon is negligible in the case of a UO<sub>2</sub> sintered product. In the case of powders and depending upon particle size, oxidation may become an important parameter if a hyper- stoichiometric uranium dioxide is used for carbide synthesis. In this case, a fraction of the carbon present will be used for the oxide reduction at rather low temperature (typically below 600°C) generating carbon dioxide gas. This effect has been proven in many previous studies [16] with the detection of CO<sub>2</sub> gas release. Therefore, the carbon addition must be adjusted to the original U/O oxide molar ratio. This ratio may be experimentally determined from a TGA oxidation cycle. However, we have chosen to introduce an additional step in the powder preparation process with an initial uranium oxide reduction through a thermal treatment at 500°C under a flowing Ar/H<sub>2</sub> gas mixture. Following the reduction thermal treatment, the actual U/C ratio of UO<sub>2</sub> was controlled by TGA. We assume than the molar ratio U/O is 2,0 +/- 0,02.

### 2.3 Synthesis conditions

As gas release is involved in the equilibrium for the UC synthesis (equation 1), an efficient CO removal enhances UC formation. Previous studies [17] have clearly proven that reducing the oxide in vacuum is an efficient way of forming UC as it displaces equilibrium 1 to the right. The reaction rate indeed decreases when the CO partial pressure increases.

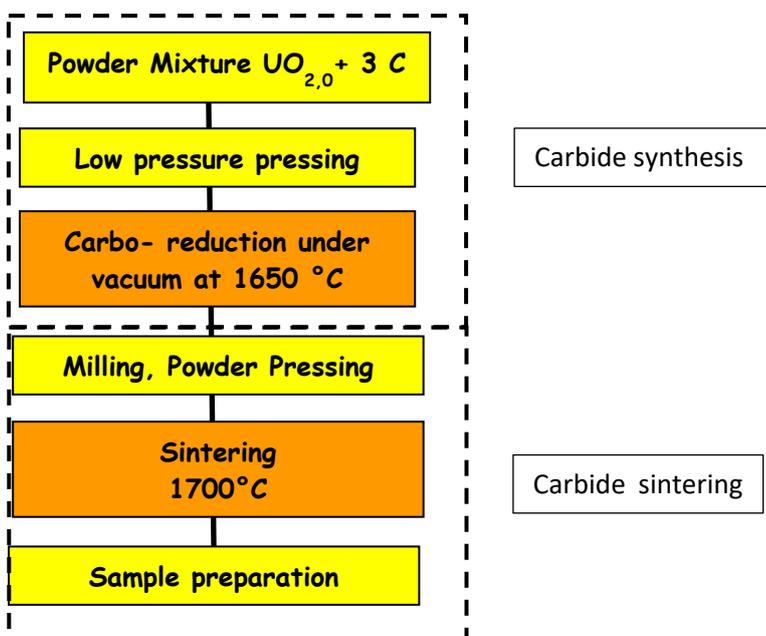


Figure 5: General process for uranium mono-carbide preparation

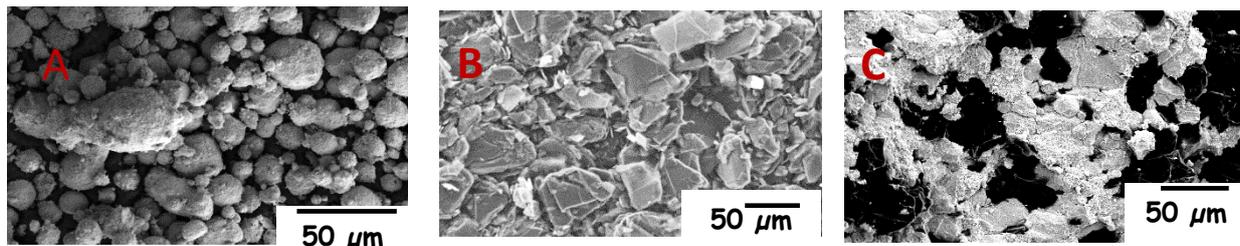


Figure 6: SEM imaging of the original  $UO_2$  (A) and graphite (B) powders and mixture of both (C) for carbide synthesis (white phase = Uranium oxide, black = graphite)

The uranium dioxide powder (see figure 6 – A) used for UC synthesis is a spray dried powder aggregates about 25  $\mu\text{m}$  diameter  $UO_2$  and with a specific area of about 3  $\text{m}^2/\text{g}$ . Following reduction of  $UO_{2+x}$  under flowing Ar/5%  $H_2$  at 500°C, dried and purified natural graphite is added in stoichiometric proportion with an average particle size of 50  $\mu\text{m}$  (see figure 5 –B). In practice, the mixture has 11.77 wt% of C. Both powders are mixed for 30 minutes in a 2 litre polycarbonate vessel using a WAB turbula® mixer. The powder is then pelletized at only 250 MPa pressure in order to get low density green pellets (see figure 5 –C – BSE image). Low density products with an open microstructure are conducive to gas release during the carbide synthesis process.

10 pellets of about 4 grams are heated under vacuum for 5 hours at 1650°C. The low vacuum pump has a capacity of 19  $\text{m}^3/\text{h}$  for a 20 litres furnace. The furnace pressure after vacuum stabilization is about 30 Pa. The heating rate is of 300°C/h at the beginning, and then it slows down to 50°C/h at 1100°C in order to minimize the pressure increase and keep the vacuum to reasonable levels. Temperature and vacuum levels are monitored during synthesis (figure 7).

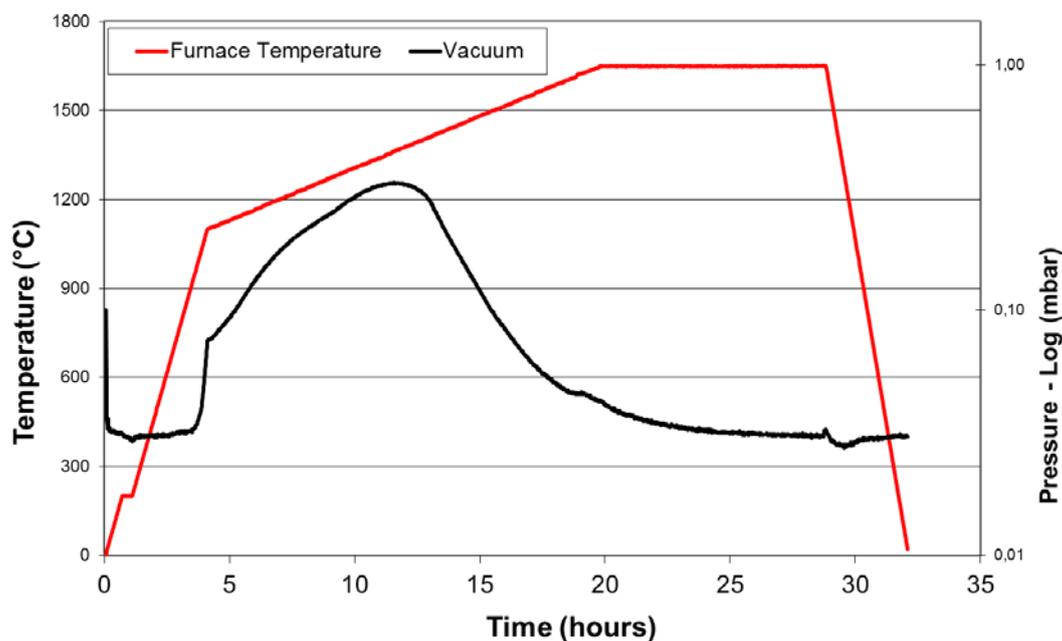


Figure 7: Synthesis under vacuum of uranium monocarbide.

The pressure evolution provides a clear indication of the onset of gas generation and therefore of the beginning of the carbide synthesis process. After going through a maximum, the pressure then decreases slowly. At 1650 °C, at the end of the plateau, the furnace pressure reaches a low level again. We have considered that the carbide synthesis is achieved at this point.

The synthesized carbide is a very porous material which has a density of only 50 % of the theoretical density (dth) (figure 8 A). The interconnecting pore structure observed in figure 8b is a clear indication of substantial gas has efficiency been released.



Figure 8: A) synthesized pellets (diameter about 8 mm) after carbo-reduction cycle and B) surface micrograph observed by SEM

To enhance sintering and to obtain carbide with greater density, carbide pellets are crushed and milled into a fine powder. A two stages milling process is necessary for powder preparation in order to get the adequate grain size. A planetary mill is used with a 250 ml WC bowl 10 mm WC grinding balls are used to grind the powder for 1 hour. It has not been possible to perform a laser particle size distribution analysis because fine carbide powder is highly pyrophoric and the laser particle size analyser does not work under a neutral atmosphere.

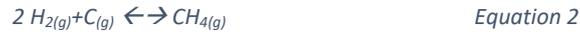
## 2.4 Influence of the sintering atmosphere

All process steps so far have been studied and optimized based on a previous study [18]. All processing parameters given picture 5 (temperature profile, final sintering temperature of 1750°C) are identical but the sintering atmosphere. The objective is to investigate the influence of the sintering atmosphere on the final material properties and in particular on the U/C molar ratio and final density. Uranium carbide may react to the gas composition especially at high temperature.

Four different sintering atmospheres have been chosen for this investigation:

- A low vacuum which has the advantage of recreating the same conditions as in the original carbide synthesis. A second carbo-reduction may induce additional oxygen removal. However, in practice, the exact sintering conditions are not totally characterized because no in site chemical analysis of the gas is connected on the residual atmosphere. The thermodynamical conditions imposed by the characteristic of the atmosphere may ultimately depend on furnace pollution.
- A high purity argon atmosphere is termed a “neutral atmosphere”. In practice, the atmospheric conditions are dependent on the purity of argon gas supply, on furnace pollution or material present in the furnace. For instance, the oxygen potential is not buffered. An on-line mass spectrometry analysis has been carried out in this case.
- A reducing atmosphere under dry Ar/5%H<sub>2</sub> which imposes a very low oxygen partial pressure of around 10<sup>-29</sup> (as measured at 650°C).
- A hydrogen/methane mixture. Because uranium carbide may form non-stoichiometric phases, it may be in principle interesting to fix the carbon potential of the gas phase during sintering in order to impose reproducible experimental conditions and possibly control the degree of non-stoichiometry. In the case of carbide sintering, the carbon chemical potential is rarely taken into account. For sintering at these high temperatures, in reducing atmosphere, either graphite isolated furnace is used, so the carbon potential is governed by the temperature, either full metallic furnace is used. In that later case, the carbon potential is not controlled. For a first attempt, we

tried to fix the carbon potential using the equilibrium methane-hydrogen dissociation (equation 2). A mixture of Argon, 4.8% H<sub>2</sub> and 2000 ppm CH<sub>4</sub> in pure argon (pH<sub>2</sub>/pCH<sub>4</sub> = 24) has been used for evaluation. This gas mixture would fix the carbon potential in the gas phase at 10<sup>-9</sup> atmosphere at 1700°C.



### 3 Sintering under different conditions

#### 3.1 Uranium carbide sintering under low vacuum

The four sintering conditions were imposed using the same equipment as that described above and using the same pellet batch with the same quantity of material (about 40 g).

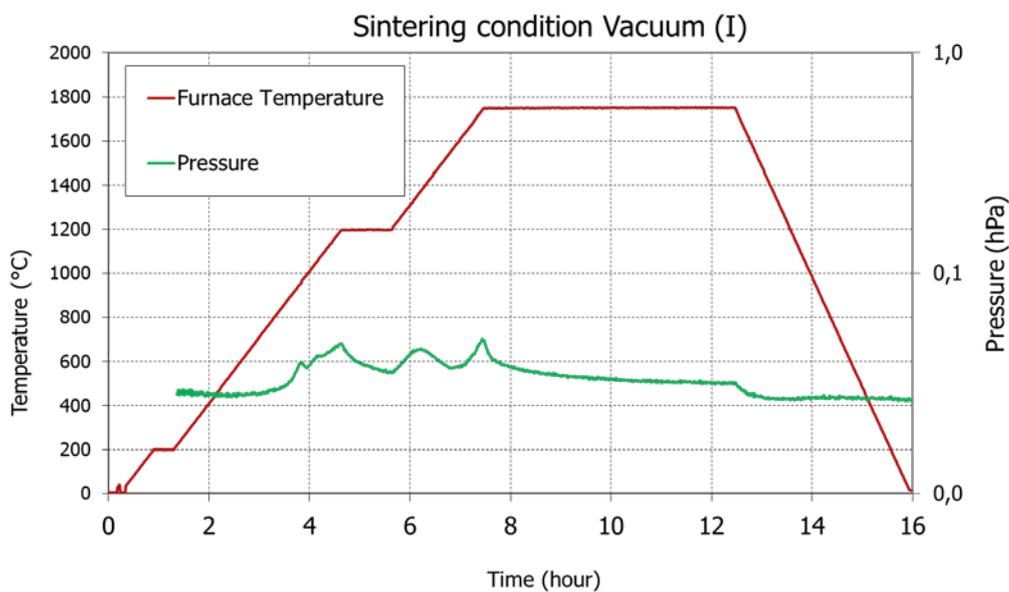


Figure 9: Sintering under low vacuum

In figure 9, the vacuum level is shown during the thermal cycle. Under low vacuum conditions, gas release clearly occurs and is illustrated by increases in pressure as a proof of a deterioration of the vacuum level. This may be interpreted as an additional carbo-reduction reaction accompanied with CO release. This may be due either to incomplete carbo-reduction process or that oxidation occurred during the powder preparation stage. This will lead to little carbon consumption in both cases and a possible U/C ratio increase in the material. The atmosphere analysis was not possible under vacuum because of the type of mass spectrometer available (The MS analyser used is designed for atmospheric pressure analysis only).

### 3.2 UC sintering involves using pure argon under atmospheric pressure

A mass spectrometer (Inficon Transpector MS) was connected to the furnace gas exhaust. This mass spectrometer is designed for gas sampling at atmospheric pressure. The MS intensity signals were quantified using reference gas cylinders for the species hydrogen, Argon, methane and carbon monoxide before the sintering investigations. However, the oxygen signal was not subjected to such a calibration process, because not expected to be present in the gas composition. This result is a clear demonstration that argon cannot be considered as a controlled atmosphere. Gas contamination or impurities will determine the real sintering atmosphere.

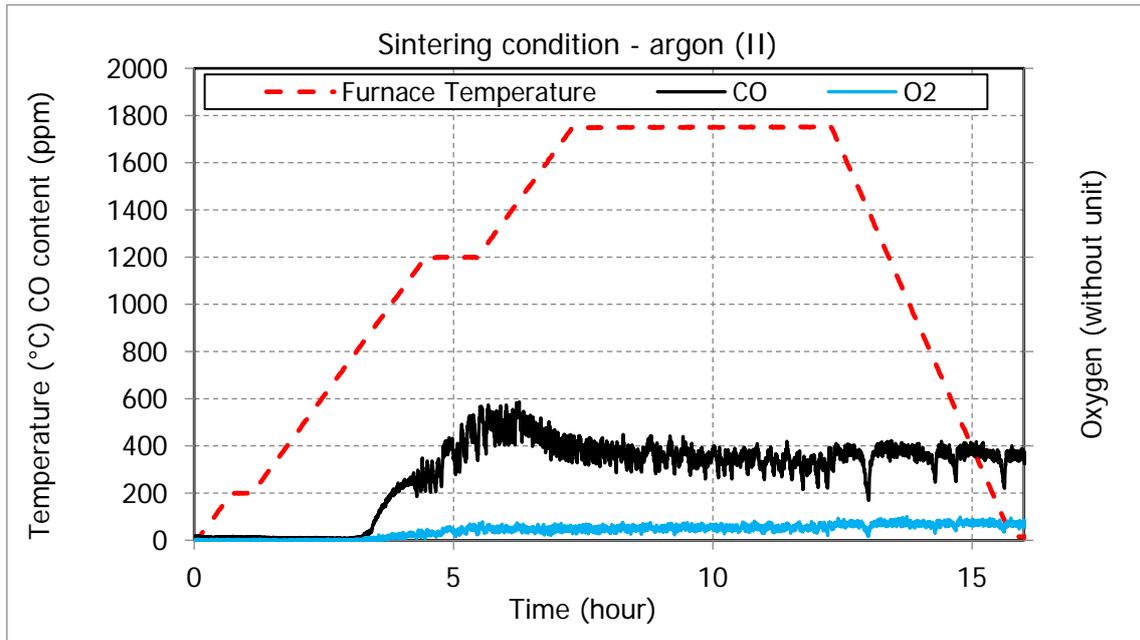


Figure 10: Carbide sintering under pure argon atmosphere

CO release is clearly observed (figure 10) during this thermal treatment and reached a steady state concentration of about 500 ppm. We can also pick up an oxygen signal (very low but above the background level). This gas analysis clearly shows that an additional reduction of an oxide by carbon to give carbon monoxide takes place during sintering. Carbon dioxide signal was not detected.

### 3.3 Uranium carbide sintering in an argon-hydrogen mixture

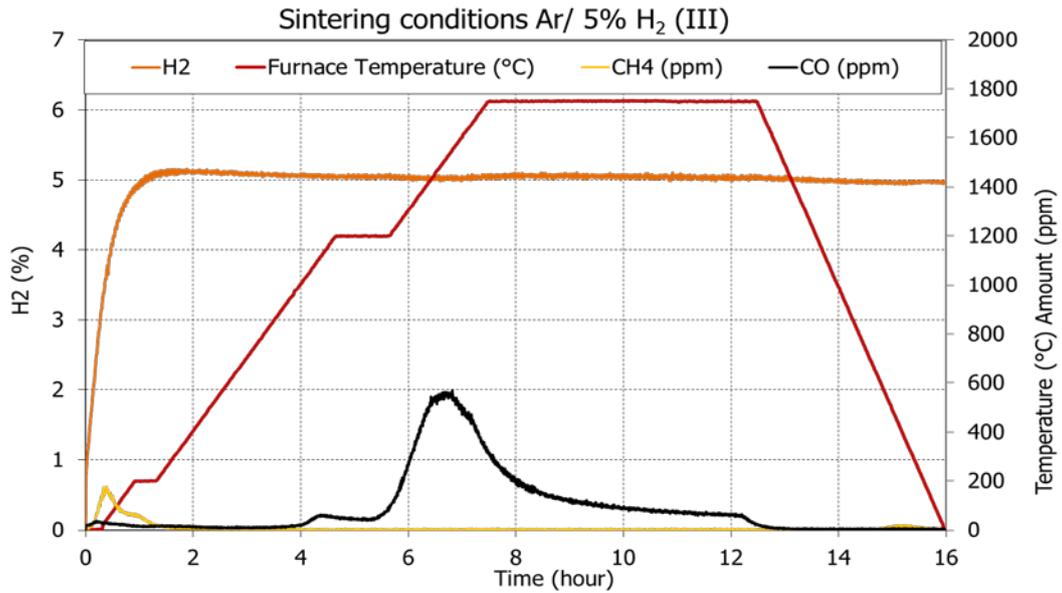


Figure 11 : carbide sintering under Ar/H<sub>2</sub> atmosphere

Under reducing conditions, using a dry Ar-5%H<sub>2</sub> mixture, the CO gas release is even more clearly detected and visible on figure 11. This gas generation could again be linked to complementary carbo-reduction reaction. Oxygen is no longer detected. The residual concentration of oxygen should react with hydrogen to give water vapour. However the water signal shows no significant evolution (not represented).

### 3.4 Uranium carbide sintering in a hydrogen/methane mixture

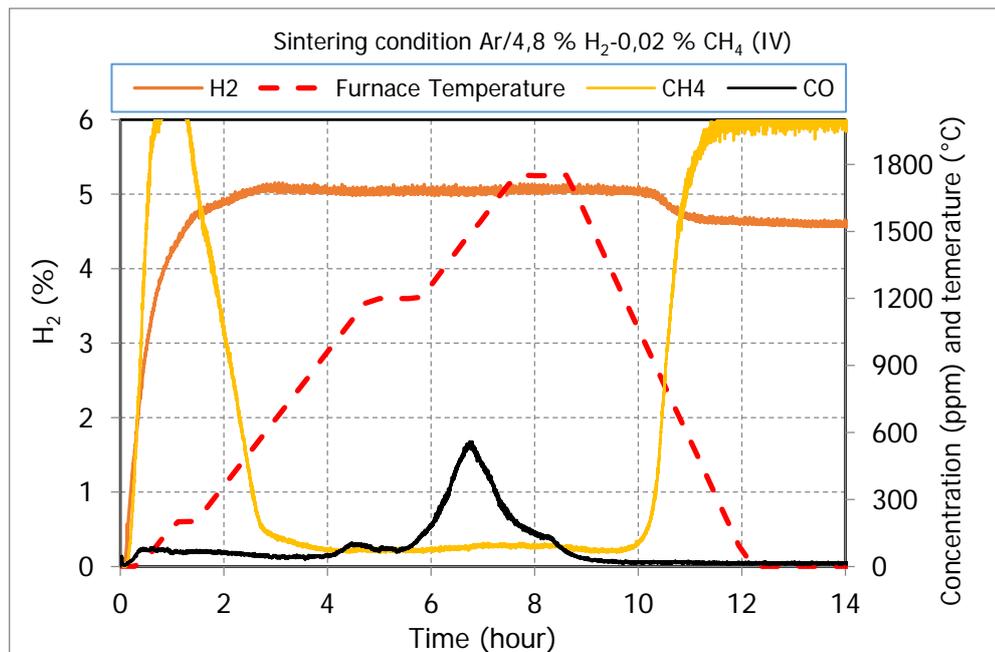


Figure 12: Sintering under gas mixture of Ar/H<sub>2</sub>/CH<sub>4</sub>

The initial furnace atmosphere at the beginning of the thermal cycle is pure argon (figure 12). An argon/hydrogen/methane gas mixture is then introduced in the oven and the expected concentration values are reached. The gas mixture chosen was 4.8 % H<sub>2</sub> and 2000 ppm CH<sub>4</sub> in argon. However, when the furnace temperature rises, at about 200 °C, the methane concentration goes down from 2000 ppm to about 50 ppm. At the end of the thermal cycle, when the temperature goes below 500°C, the gas composition is again as introduced in the oven at the expected concentration.

## 4 Characterisation of the sintered pellets

### 4.1 Sintered Samples microstructure

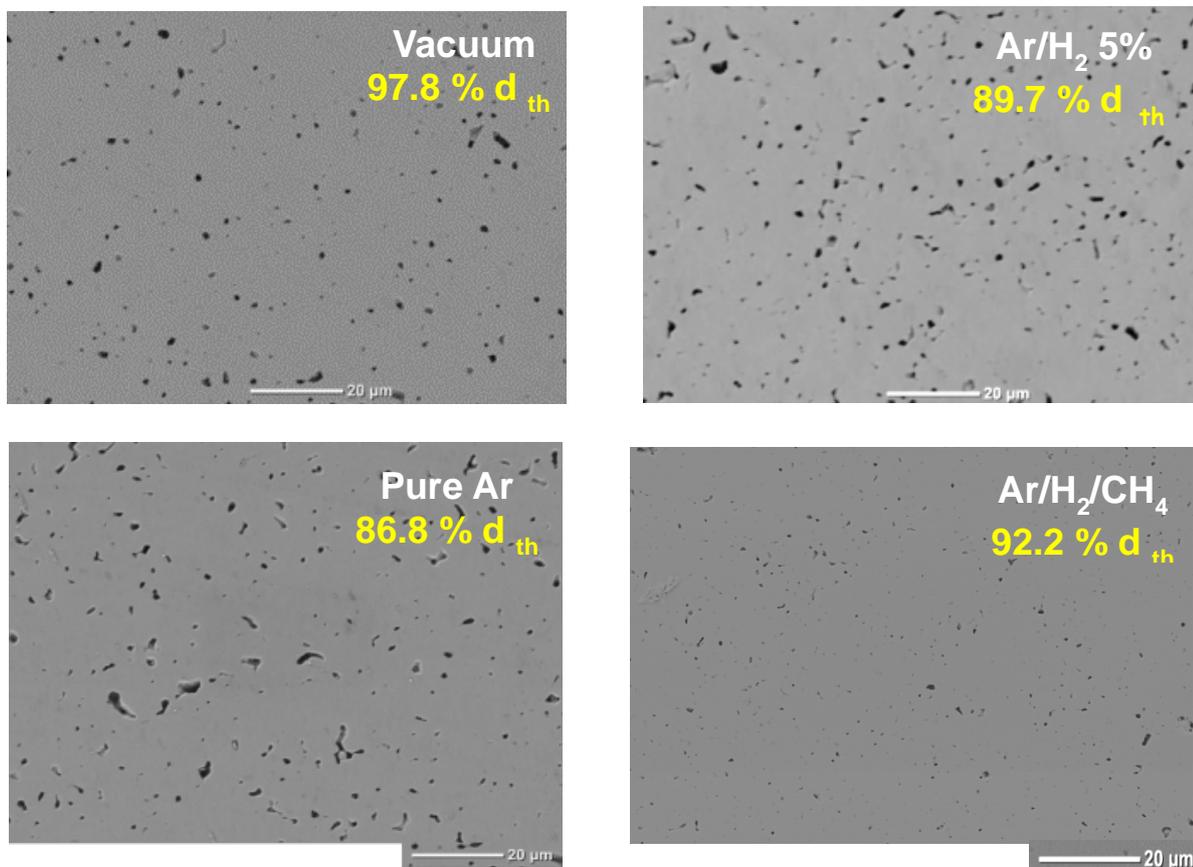


Figure 13: SEM Samples porosity after surface polishing depending of the sintering conditions

Sample microstructures (figure 13) show dense products. The total porosities are visually lower for both low vacuum and Ar-H<sub>2</sub>-CH<sub>4</sub> sintering conditions.

### 4.2 Porosity and apparent density

Figure 14 summarizes the density and porosity measurements performed on samples obtained using different sintering conditions. The data are resumed in table 1. Measurements have been made on 5 pellets of each condition following a procedure of immersion in Limonene (C<sub>6</sub>H<sub>10</sub>). The use of a liquid hydrocarbon instead of

ethanol is precluded due to the possible presence of water in ethanol. Limonene is also an oxygen free compound which seems to be better to prevent carbide oxidation.

The apparent density is obtained from the measurement of the pellet dimensions and volume calculation. Hydrostatic density measurements which exclude the volume contribution of open pores provides higher values.

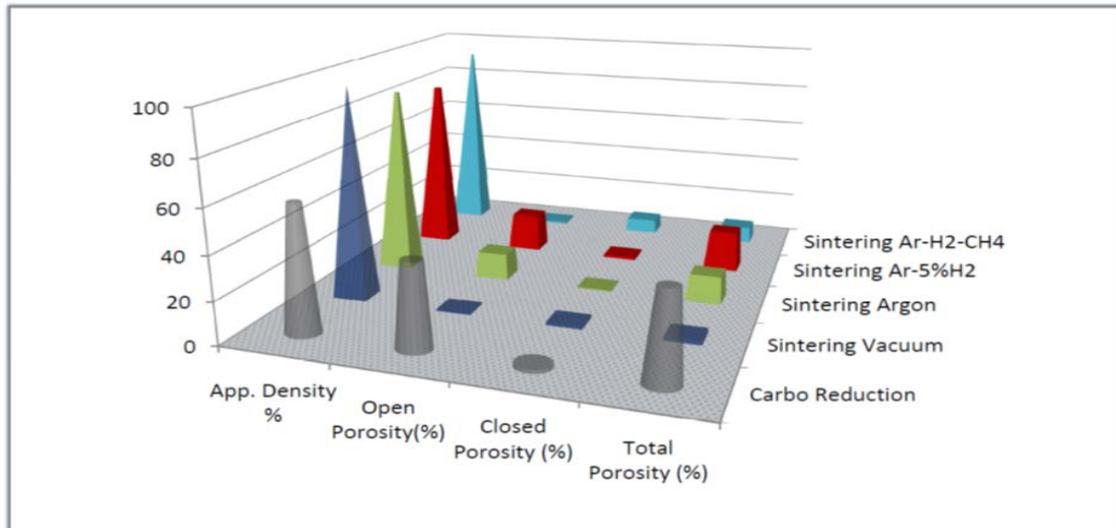


Figure 14: Average densities and porosities of the samples depending of the sintering conditions. Data from carboreduction samples are given for comparison.

Figures 14, the properties of the sintered pellets are reported and for comparison the results of pellets obtained after carboreduction. After carbo-reduction, the pellets apparent density is about 50% dth and the porosity is almost totally open.

Two sintering conditions lead to densities above 90%: a sintering under vacuum or a sintering with a mixture of Hydrogen/methane.

The samples obtained after sintering under vacuum have the highest apparent density and the lowest total porosity. This result may be explained in relation with the sintering conditions. Gas generation during sintering is always a possible source of porosity formation. CO can be easily removed under vacuum which is conducive to densification. The use of an Ar-H<sub>2</sub> and CH<sub>4</sub> mixture also appears to lead to a dense material certainly denser than when using argon-hydrogen. The presence of methane appears to be conducive sintering possibly because in this case the carbon potential induces higher cation diffusion coefficients.

Table 1: Apparent density and hydrostatic density

Theoretical density of UC dth = 13.62		
Sintering conditions	Apparent density (g/cm <sup>3</sup> ) σ = 0.2	Hydrostatic Density g/cm <sup>3</sup> (% of theoretical density)
Sintering: low vacuum	12.53	13.33 (97.8%)
Sintering: pure argon	11.47	11.83 (86.7%)
Sintering: mixture Argon 95%-H <sub>2</sub> 5%	11.89	12.23 (89.7%)
Sintering mixture Ar-H <sub>2</sub> -CH <sub>4</sub>	12.35	12.57 (92.2%)

### 4.3 Oxygen content and U/C final molar ratio

#### 4.3.1 Determination of samples oxygen content

The main objective was to manufacture samples with the lowest possible oxygen content and a controlled carbon content, corresponding to a composition as close to stoichiometry as possible. During the manufacturing process, oxygen is inevitably incorporated as an impurity. Oxygen concentration values were obtained using a TC600 equipment from LECO®. The determination is based on high temperature sample fusion (up to 1800°C) in reducing conditions. The oxygen content is calculated from CO and CO<sub>2</sub> gas emission quantified by IR absorption. For preparation purpose, the samples are crushed and milled in inert atmosphere. Because, the oxygen analyser is in another nuclear facility, a closed gastight packaging is needed for sample transportation and sample storage. The time elapsed between sample preparation and measurement was approximately two weeks. Table 2 summarises the oxygen content in the different samples. The oxygen levels are quite high compared with demanded specifications that are less than 1000 ppm. At first sight, no clear correlation can be found between the sintering conditions and sample oxygen content. The oxygen content after synthesis by carbo-reduction is about 3500 ppm. A small decrease is observed for vacuum and pure argon sintering conditions.

#### 4.3.2 Determination of U/C ratios by Thermogravimetric Analysis (TGA)

Samples are first crushed into small fragments in an inert glove box. Fragments should not be too small in order to avoid spontaneous oxidation before measurement in air. The carbon content determination is calculated from the complete carbide oxidation under dry air mixture.

The complete oxidation reaction of UC<sub>x</sub> considered is the following (equation 4):



Taking for assumption that the final product is a pure U<sub>3</sub>O<sub>8</sub> compound, the U/C ratio in samples is calculated from the following relationship:

$$C/U = 1/x = (M_{U_3O_8} / (3(\Delta M/M + 1) * M_c) - (M_u/M_c)) \quad \text{Equation 4}$$

Notations used :

X: molar quantity of carbon in UC

Mu: uranium molar weight

Mc : carbon molar weight

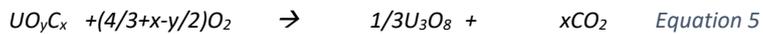
$M_{U_3O_8}$ : uranium oxide molar weight

$\Delta M/M$  : final relative mass loss.

The calculated U/C ratios (table 2) are within the range of a single mono carbide phase.

#### 4.3.3 Accounting for the presence of oxygen in the original carbide powder

The oxygen content in samples is known and a correction in the U/C calculation can be introduced by considering  $UO_yC_x$  as the initial carbide formulation. The complete carbide oxidation reaction can be written as equation 5:



The carbon content is then calculated taking into account the sample oxygen content. The U/C ratios after correction are reported in table 2.

All calculated U/C molar ratios are above 1 after correction. These U/C values mean a small carbon deficit in the carbide composition. After sintering, it seems logical to get a larger carbon deficit because of the observed CO production. The results however are very close and taking into account the relative uncertainty of the TGA determination, the influence of the sintering conditions on the U/C ratio is difficult to establish.

Table 2: total oxygen content in samples measure by LECO and U/C ration determination by TGA

Sintering conditions	Total oxygen content (ppm) +/- 100 ppm	TGA $\Delta M/M$ %	U/C ratio – TGA (objective U/C =1) +/-0.02	U/C ratio after correction +/-0.02
After carbo-reduction	3510	12.344	1.015	1.085
I - Vacuum	2150	12.557	1.057	1.111
II - Argon	2600	12.237	0.995	1.052
III - Ar/H <sub>2</sub> 5%	6300	12.192	0.987	1.134
IV - Ar/H <sub>2</sub> -CH <sub>4</sub> 5%	3750	12.125	0.974	1.056

## 5 Discussion on the sample properties depending on the sintering conditions

The carbides stoichiometry and composition may closely depend on the sintering atmosphere. If a thermodynamic equilibrium is set, the composition may be reproducible and predictable by the calculation. Uranium carbides have been widely

Sintering with low vacuum is an unstable thermodynamic condition. Uranium carbide will continuously try to reach equilibrium and evaporate.  $UC_xO_y$  will evaluate to  $UC_x$  compounds.

We can take into consideration the work of Tetenbaum and Al on the measurement of carbon activity over  $UC_x$  compounds [19]. Other work of Anthonysamy [20] can be taken into consideration but refers to U-Pu-C-O-N compounds.

Our attempt to control the oxygen partial pressure and the carbon activity gives rise of many technical difficulties. As already mentioned, the current sintering conditions used (vacuum, neutral gas and reducing by argon-hydrogen) are far too unspecified to give clear indication on real sintering atmosphere. To get the assurance of partial pressure control, gas equilibrium has to be fixed by gas equilibrium.

The gas mixture used for carbon partial pressure buffering gives a particular gas profile in temperature (see figure 13). A blank test performed in the same conditions (figure 15) without the carbides reveals the same temperature dependence in gas concentration profile.

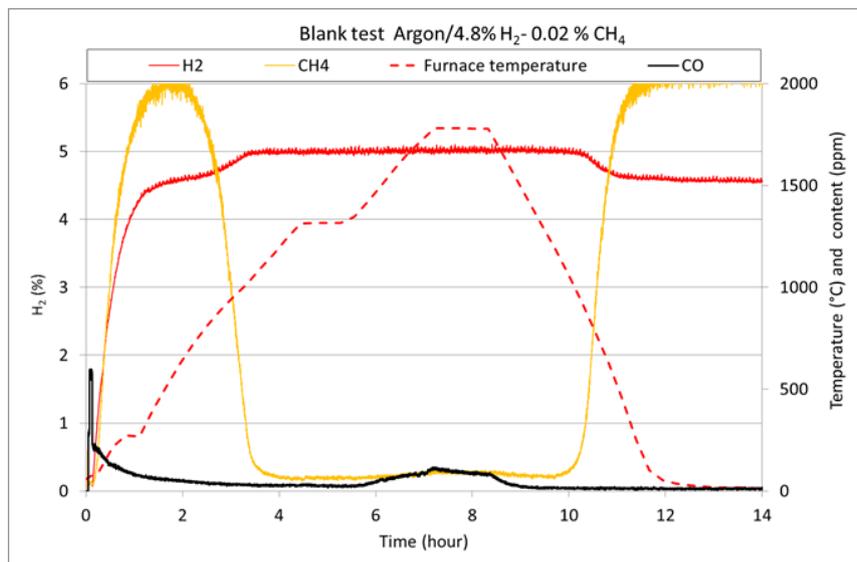


Figure 15: Gas analysis during a blank test

Thermodynamic calculations performed with the Factsage® 7.0 software (Database SGPS-SGTE –pure substance V13-1, 2013), confirm the observed phenomena. Methane above 500°C, dissociates into  $H_2$  and carbon (gas and solid) (see figure 16) obtained from thermodynamical calculations from the gas mixture use for sintering (Ar-5%  $H_2$  + 0.02% $CH_4$ ).

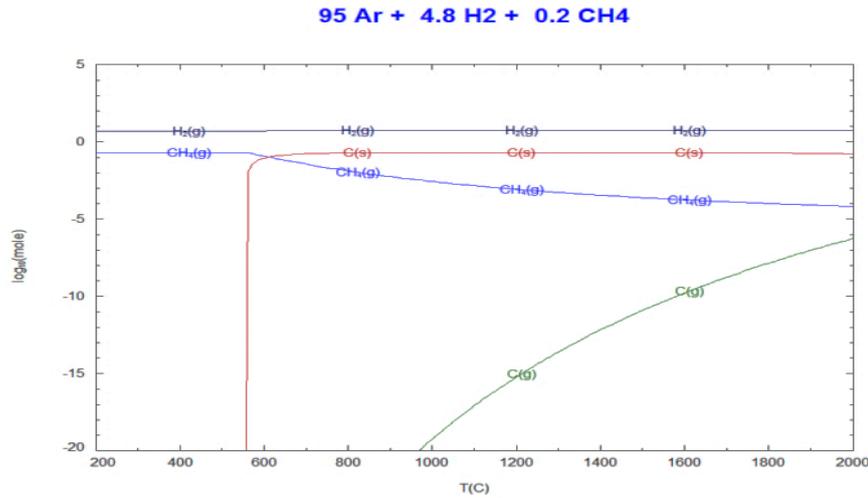


Figure 16: Equilibrium calculation of the sintering atmosphere as a function of the temperature (Factsage) C(s) –solid carbon; C(g) - gas phase carbon.

Carbon becomes then available in solid form and the carbon partial pressure (C(g) in figure 16) increases.

At 1700°C, the carbon activity is of about  $10^{-9}$  as it can be read on figure 16. The metallic furnace used for this investigation has many tungsten elements (heating elements, shields and support plates) that are liable to react at high temperature with whatever amount of carbon present in the gas phase. As a result of this, the buffering reaction involving hydrogen and methane (equation 2) is likely to be disrupted and the tungsten, tungsten carbide equilibrium may predominate. The carbon potential reaction buffering should be driven by the reaction described (equation 3). However, as it has been described, gas mixture containing methane seems to have a positive influence compared to simple Ar/H<sub>2</sub> mixture on densification. The available carbon given from the methane dissociation and the carbon partial pressure may play a role in densification. Gaseous carbon may help to reduce a probable oxide layer at the surface of carbide and enhance sintering.



The inconvenience of using methane in a metallic furnace is the partial conversion of the tungsten into brittle tungsten carbide. This phenomenon is well known and occurs gently during furnace service and finally causes the deterioration of the tungsten components of the furnace. The use of methane may accelerate the phenomenon.

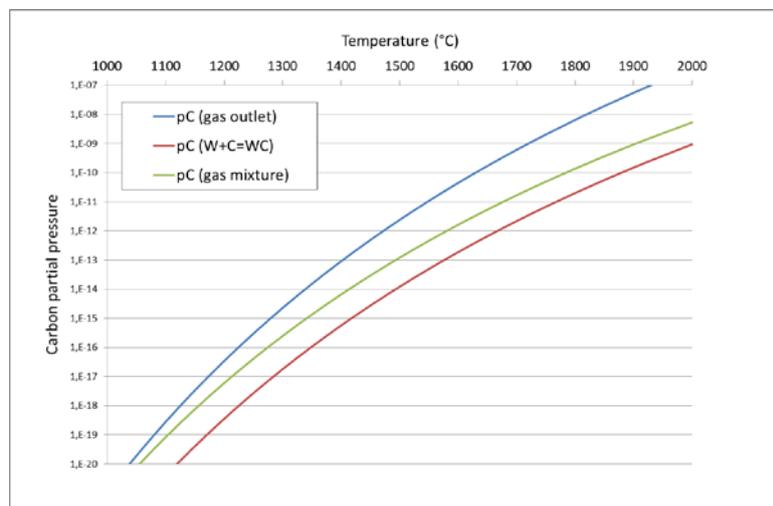


Figure 17: Carbon partial pressure calculate with several hypothesis

Moreover, the carbon partial pressure has been calculated from the equilibrium  $C+W \rightarrow WC$  (equation 3) and compare with the inlet gas mixture (figure 16) and the outlet gas for temperature from 1000 to 2000°C.

The carbon partial pressure due to the tungsten is always the lowest one. It means that the carbon pressure will be controlled by the equilibrium of equation 3.

## 6 Conclusions

Process optimization has been investigated in order to obtain a dense, single phase uranium carbide material after sintering. The manufacturing of uranium mono-carbide requires the development of adapted equipment and the use of a strict protocol. The final U/C ratio which in turn determines a large range of material properties is very much dependent upon sintering conditions and it is recommended this be done by adjustments in the carbon potential during sintering. Because of possible incorporation of impurities, particularly oxygen, all stages in the process have to be optimized and carried out in a high quality inert atmosphere. The influence of four sintering atmospheres has been studied; sintering under low vacuum, under pure argon, under argon – 5 % hydrogen and finally argon- hydrogen-methane for a test of carbon potential control. The denser material was obtained sintering under vacuum or with a mixture of hydrogen and methane.

Starting from a mixture of stoichiometric  $UO_2$  and three times the amount of carbon, in order to obtain UC compound, all sintered samples present a small carbon deficit. The oxygen content in all samples remains higher than the expected value (1000 ppm as specified). However, sample may be use for material investigation on original technics [21]. The influence of hydrogen-methane gas is not entirely understood. The methane concentration in a metallic furnace is not controllable because of methane dissociation and the primary carburization of the furnace internal metallic parts.

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