Experimental report

08/12/2020

Proposal: **1-01-168** **Council:** 4/2019

Title: In situ study of reactive sintering in U+Si compacted powders to formthe U3Si2 compound.

Research area: Materials

This proposal is a new proposal

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Samples: U + Si

Instrument	Requested days	Allocated days	From	To
D20	4	3	14/01/2020	17/01/2020

Abstract:

Studies are performed worldwide to convert Research Reactors to low enriched uranium fuel. The U3Si2 compound is one of the main candidates. U3Si2-based fuels correspond to micrometric particles dispersed in an Al matrix, to form a fuel core that is cladded to obtain a fuel plate by rolling. U3Si2 is usually synthesized by melting-solidification. The so obtained ingot is crushed, leading to powder particles that are difficult to control in terms of size and shape. It induces a limitation of the volume fraction of U3Si2 particles in the fuel core. New process routes, allowing to customize the particles to make them more suitable for rolling, are currently studied. Julien Havette's thesis comes within this framework. He developed an innovative process based on reactive sintering of compacted powders of U and Si, to obtain a porous U3Si2 pellet which can be easily powdered. In-situ neutron diffraction would allow (i) to follow the bulk solid-state reaction and thus, optimize the heat treatment conditions to find a compromise between reaction kinetics and densification and (ii) to acquire a better knowledge of the U+Si binary system and of the formation of U3Si2.

During experiment n°1-01-168, performed in January 2020, the solid-state formation of U_3Si_2 from U+Si compacted powders was followed in situ using neutron diffraction on D20 high-intensity two-axis diffractometer. Experiments were carried out using a Ge (115) monochromator, which gives a wavelength λ=1.54 Å. A 90° take-off angle was used to have a compromise between flux and resolution. Diffraction patterns were taken in the range 0.42 – 150.77° (2θ) with a 0.05° step. As the objective of these experiments was to follow phase transitions, data collection durations were 600 s per pattern for the first and second experiments and of 60 s for the third one.

Pellets of uranium and silicon powders were pressed and placed in cylindrical stainless steel sample holders (9 g each). Compacted powders could not be exposed to air, as they are highly pyrophoric. Dedicated stainless steel sample holders were made and connected to a valve. Thanks to these airtight sample holders, samples were kept under inert atmosphere from their production to their analysis by neutron diffraction. Sample holder were placed inside the D20 furnace with vanadium heating element.

Diffraction data sets were analysed using Fullprof Suite. Data were refined applying the Rietveld method. A systematic refinement method was applied, using sequential mode. Mass fraction of each phase is estimated at each temperature. This way it allows following the reaction progress.

Three days of beamtime have been allocated on D20 to perform three different experiments:

First experiment conditions and results

The first experiment aimed at heating the sample with a slow ramp in order to follow phase transition. A slow heating ramp at 50 K.h^{-1} was applied. At 1000 K, the heating element broke and the temperature fell down to room temperature. Heating element was changed and the temperature was quickly increased to 950 K. In order to optimize allocated beam time, the heating ramp was changed to 200 K.h^{-1} up to 1190 K. The temperature was maintained for one hour before natural cooling.

Refinements allow displaying mass fraction of each phase as a function of temperature (**Figure 1)**. Each point represent mass fraction of each phase determined on a neutron diffraction pattern with 10 minutes long acquisition.

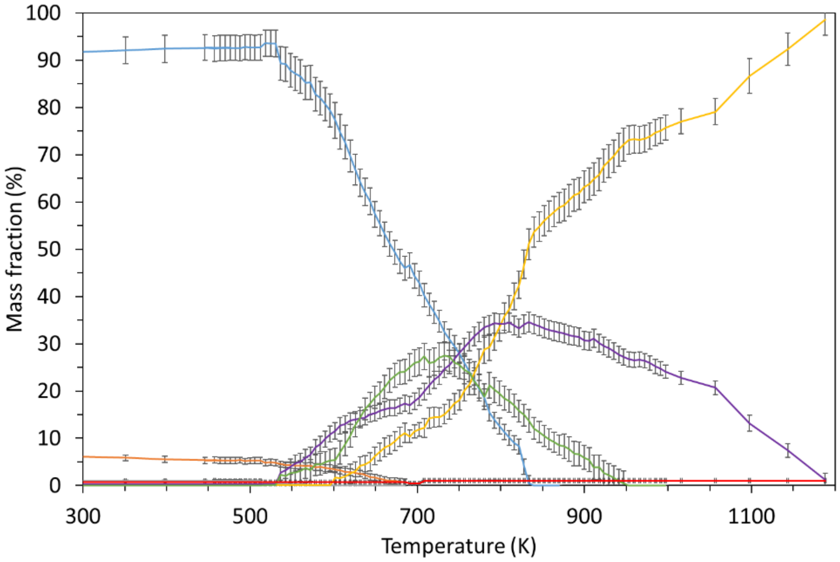

Figure 1 : mass fraction evolution as a function of temperature, determined by refinement with the Rietveld method on 10 minutes neutron diffraction pattern acquisition, with ●U ●Si ●UH_3 ●U_3Si ●U_3Si_5 ●U_3Si_2 and ●UO_2

We first index αU and Si as majority phases. Silicon mass fraction starts to decrease at 475 K while αU at about 525 K. αU has linear decrease and no more free uranium can be indexed at 825 K. Consequently, several silicides are formed starting with U_3Si at 525 K and U_3Si_5 at 535 K. U_3Si_2 first appears at 600 K. U_3Si_5 mass fraction quickly increases to reach a maximum of 27%wt. at 700 K. U_3Si mass fraction also increases to reach a maximum of 34%wt. at 775 K. The decrease of those two phases indicate homogenization of the composition.

The complete homogenization of the sample is reached at 1175 K as only U_3Si_2 and about 1%wt. UO_2 can be quantified. UO_2 is probably coming from oxygen impurities.

However, after cooling to room temperature, U_3Si and αU most intense reflections reappears (**Figure 2** and **Table 1**). The reappearance of those two phases is still under investigation.

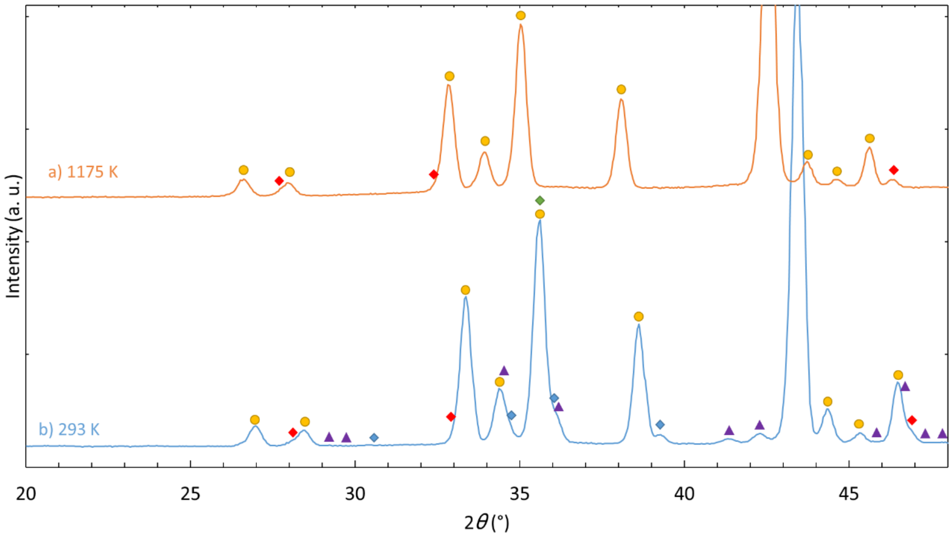

Figure 2 : neutron diffraction pattern acquired on U+Si sample heated at (a) 1175 K and (b) after cooling at room temperature, indexed with ◆αU ▲U_3Si ●U_3Si_2 and ◆UO_2

Table 1 : phase quantification determined by refinement with the Rietveld method on the diffraction pattern displayed in Figure 2, and goodness of fit associated

Temperature (K)	U_3Si_2 (%wt.)	UO_2 (%wt.)	U_3Si (%wt.)	αU (%wt.)	Rp (%)	Rwp (%)	χ^2
1190	98.9 ± 0.5	1.0 ± 0.1	0	0	10.6	9.31	35.07
293	86.3±0.7	0.9 ± 0.1	4.3 ± 0.7	8.5 ±0.4	8.45	9.09	69.33

Second experiment conditions

According to the first experiment, numerous phenomena take place at temperature between 775 and 875 K. U_3Si_2 seems to be the majority phase at about 850 K. Consequently, we wanted to know if kinetics of the reaction allowed its completion at this temperature in the aim of saving energy.

Short plateau of 1h were maintained every 50 K in order to see at which temperature important phase transitions happen. We observe that homogenization of the composition begins at 850 K. This temperature was maintained for 13h. Evidencing that homogenization does not progress anymore, a temperature increase was applied to check if it could be possible to reach full homogenization.

Figure 3 displays the mass fraction as a function of time and temperature. The temperature of each point is displayed in red dots on the secondary y-axis. Temperature at which the first silicides are formed is consistent with the one observed on experiment 1. However, during the long hold at 850 K we can see that the reaction does not progress anymore and that the sample is composed of U_3Si_2 (about 79%wt.), U_3Si (about 11%wt.), U_3Si_5 (about 8%wt.) and perhaps o-USi (3%wt.). For the latter phase, its indexation is difficult due to the low intensities of corresponding reflections.

Third experiment conditions

With the aim of energy and time saving, it could be interesting to perform this reaction as fast as possible. The second experiment allowed us to see that after a long time at 850 K the completion of the reaction was not reached.

The sample was heated very quickly in order to confirm the hypothesis that the reaction is temperature governed. To be able to follow phase transition, acquisition were shortened to 60 seconds during the heating ramp. The furnace allows to heat from room temperature to 1075 K within 2 minutes. Observing that majority of changes already took place and that sample evolution becomes slow, diffractogram acquisition time was set to 10 minutes. After a heating ramp, up to 1130 K, was performed, the temperature plateau was kept for 2.5 hours. The reaction having reached equilibrium, a slow cooling ramp was set at 82 $K.h^{-1}$.

At room temperature U, Si are indexed (**Figure 4**). After only 60 s, that allows reaching 900 K, almost all silicon has reacted (no more reflection at 30°) and many silicides are already formed. After 12 minutes at 1060 K, U_3Si_2 is already the majority phase. This temperature is maintained during 30 minutes and it can be seen that the reaction becomes slow. This led us to increase the temperature slowly (50 $K.h^{-1}$). At 1130 K only U_3Si_2 is indexed. The fast heating allowed observing that it is possible to reach the same reaction progress as the experiment 2 (after 12h at 575°) in ten minutes. Si diffusion in particles is very fast. However, homogenization of the composition at the scale of the sample requires higher temperature.

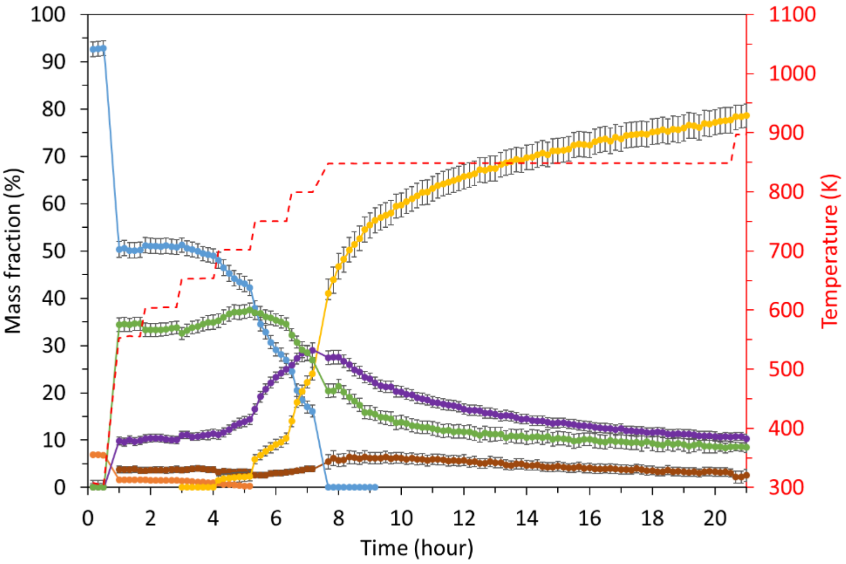

Figure 3: mass fraction evolution as a function of time, determined by refinement with the Rietveld method on 10 minutes neutron diffraction pattern acquisition, with ● U ● Si ● UH_3 ● U_3Si ● U_3Si_5 ● U_3Si_2 ● o-USi and temperature evolution on the secondary y-axis in red dotted line.

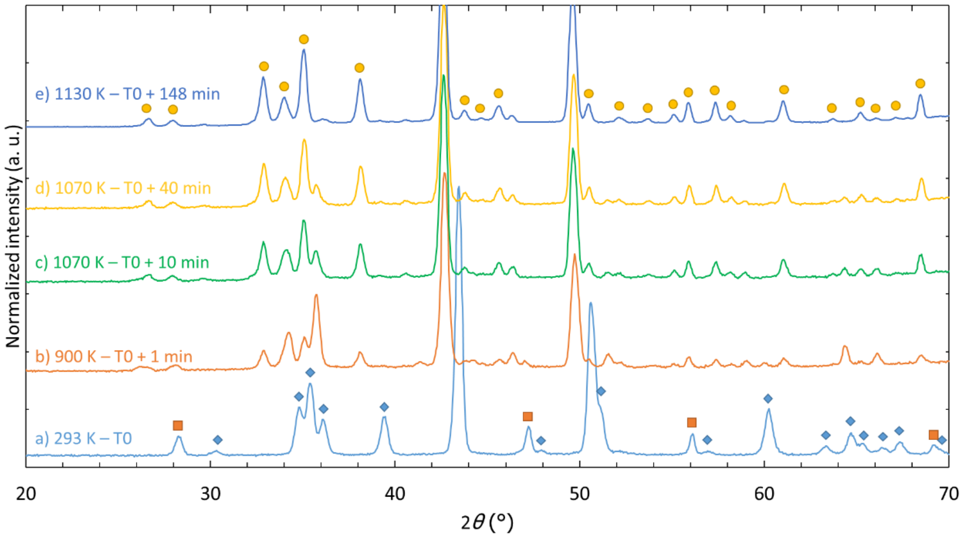

Figure 4: neutron diffractograms acquired during fast heating ramp, indexed with ◆ U ■ Si ● U_3Si_2 patterns

Complete analysis and interpretation of the whole set of neutron diffraction data is still underway, as well as the microstructural characterization of the three resulting samples.