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Review

Pyrophoric behaviour of uranium hydride and uranium powders

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ABSTRACT

Thermal stability and spontaneous ignition conditions of uranium hydride and uranium metal fine powders have been studied and observed in an original and dedicated experimental device placed inside a glove box under flowing pure argon. Pure uranium hydride powder with low amount of oxide (<0.5 wt.%) was obtained by heat treatment at low temperature in flowing $Ar/5\%H_2$. Pure uranium powder was obtained by dehydration in flowing pure argon. Those fine powders showed spontaneous ignition at room temperature in air. An in situ CCD-camera displayed ignition associated with powder temperature measurement. Characterization of powders before and after ignition was performed by XRD measurements and SEM observations. Oxidation mechanisms are proposed.

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1. Introduction

In order to investigate uranium (metal) and uranium compounds behaviour under oxidizing atmosphere, CEA research has already concerned uranium mononitride and uranium monocarbide powders reaction in flowing air and argon or nitrogen with different amounts of oxygen [1,2]. Parameters as grain size, heating rate, temperature and elaboration conditions have been studied. Such powders often show pyrophoric behaviour, sometimes at low temperatures [3,4].

Further studies are now going on concerning other uranium-base powders especially uranium hydride and fine uranium powders obtained from UH_3 thermal dissociation. Synthesis conditions in the range of several grams and powder characterization are first described. Handling uranium hydride imposed working in an inert atmosphere, with very low amounts of oxygen and moisture, because of its extremely high thermal instability and its ignition under oxidizing atmospheres. Experimental device was specifically set up in order to maintain amounts of UH_3 or U powders under pure inert gas and to carry out ignition tests on several grams under controlled atmosphere, without pre-oxidation.

The originality of the present study consists in the thermal instability of fine powders and their spontaneous ignition in air

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being observed with a CCD-camera placed above the crucible outside the furnace. Sample temperature was measured with thermocouples directly placed inside the powder layer.

The synthesis conditions of UH_3 powders such as temperature, gas composition, flow rate, processing time, are not well based. Hausner and Zambrow [5] indicates 175–225 °C temperature range as an optimal level for obtaining pure uranium hydride in flowing pure hydrogen. Small amount of oxygen in hydrogen process gas is known to delay the start of the reaction. Maximum reaction rate lays around 225 °C. Higher reaction rates can be obtained with higher hydrogen pressures. Above 225 °C, hydration kinetics become progressively lower and uranium grains obtained by decomposition of hydride may appear under vacuum. At higher temperature, uranium particles formed during decomposition of hydride may sinter in vacuum.

The reverse reaction between uranium and hydrogen becomes significant above 225 °C for Stakebake [6]. Albrecht and Mallett [7] shows maximum reaction velocity at about 280 °C and Hashino and Okajima [8] indicates 268 °C as a limit temperature. Rate decrease at higher temperatures is due to decomposition reaction hindering the hydration reaction process. Alire studies [9] show that induction times could be eliminated by using high purity gases. Induction effects caused by surface oxide films may be eliminated in high vacuum [10]. Furthermore, Condon [10] indicates dehydration kinetics in the range 200–300 °C. Many studies have been done with uranium bulk material. Hashino [8] and Condon [10] studied uranium coupons.

Uranium hydride occurs from following reaction:

$$U + 3/2H_2 \rightarrow UH_3, \quad \text{with } \Delta Hr = -127\ \text{kJ mol}^{-1}$$

This reaction is reversible and decomposition of UH_3 can occur under specific conditions.

2. Materials and experimental device

Uranium base-material was used in the form of small thin millimetric plates about 20 mg each. After treatment in nitric acid 3.5 N solution during 12 min to avoid oxide-scale on uranium surface, the plates were exposed to flowing 0.5 L min^{-1} argon containing 5% hydrogen, during 10 h at 192 °C. Temperature was reached with a rate of 10 °C min^{-1}. Platelets were hydrated in a stainless steel 30 mm diameter crucible which was heat-treated in argon during 4 h at 300 °C before hydration to avoid oxygen pollution. In those conditions quantitative hydration of uranium metal could be obtained for sample mass around 5 g.

Fine uranium powder could be obtained by heat treatment of previous UH_3 powder in the same flowing conditions but in pure argon, during 10 h at higher temperature 250 °C, allowing dehydration. A 30 mm diameter crucible was used as for UH_3 synthesis.

Both experiments were performed inside a kanthal-resistor furnace allowing maximal temperature of 500 °C. The furnace was placed inside a glove-box with very low leak rate $<5.10^{-4}\ h^{-1}$. Glove-box was maintained in flowing pure argon recycled with an inerting unit after removal of oxygen and water vapor. Two purification reactors (purification reactor consisting in a molecular sieve for water vapor and in copper for oxygen impurity) allowed very small concentrations ranging between 2 and 8 ppm. This experimental specificity was necessary for handling fine reactive powders as uranium hydride to prevent them from oxygen before controlled heat-treatment in the furnace. It allowed obtaining very small amounts of oxide in UH_3 and U powders.

Ignition tests were performed in the same furnace under different oxidizing atmospheres and especially in air. Samples were exposed to flowing gas rates until 10 L min^{-1}. Round 2 g of uranium

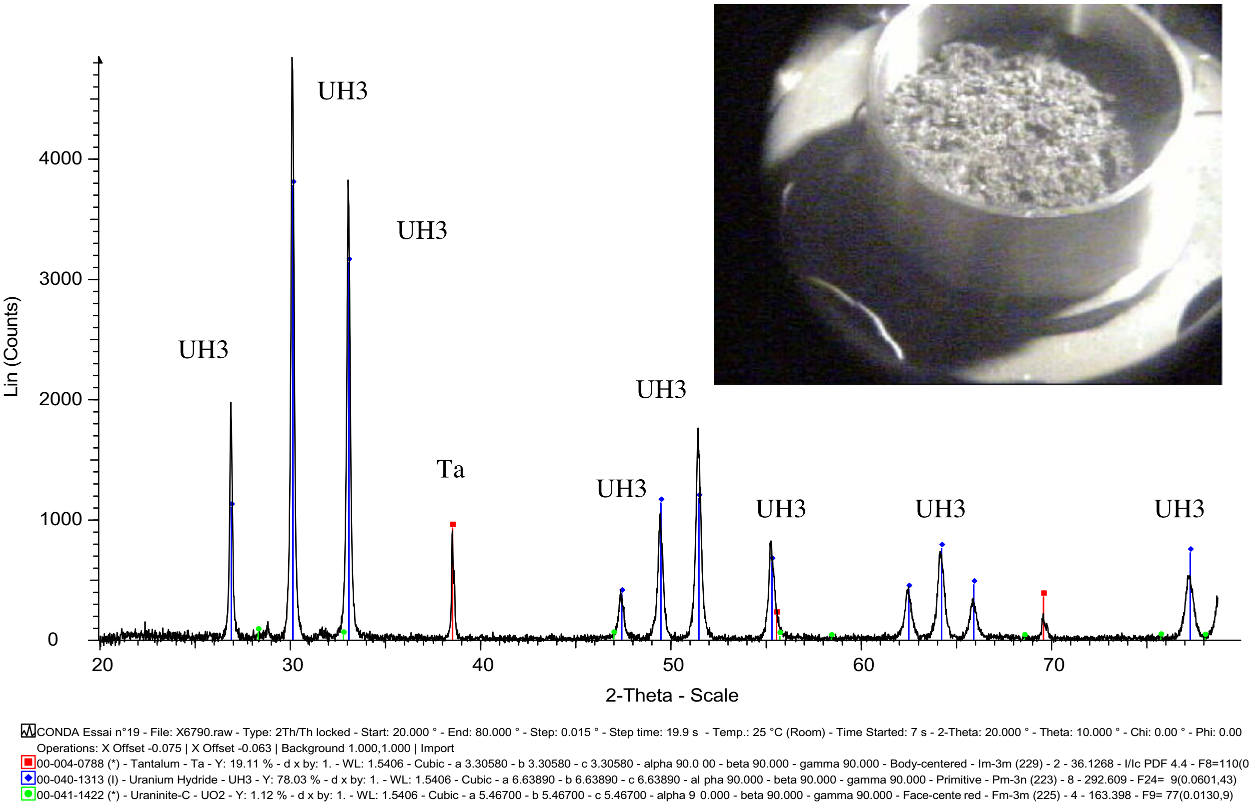

Fig. 1. Uranium hydride powder obtained after heat-treatment of uranium plates in Ar–5%H_2 and XRD analysis.

hydride or uranium powder was placed inside a stainless steel 15 mm diameter and 0.2 mm thick crucible. The experimental device allowed viewing material behaviour during heating and ignition through viewports and registering with a CCD camera. Continuous temperature measurements at various points of the powder were registered with K-thermocouples placed inside the sample. A two-color optical pyrometer was used to measure sample surface temperature in the range from 1000 to 3000 °C. Pressure measurement inside the furnace was also registered. The sample was heated at 5 °C min^{-1} up to 500 °C, after which the temperature was maintained constant at 500 °C during 30 min before cooling at 10 °C min^{-1} down to ambient temperature.

3. Results

3.1. Synthesis of pure uranium hydride

After heat treatment under flowing Ar/5%H_2, uranium plates were transformed into a fine black uranium hydride powder. Quantitative hydration of uranium metal could be obtained for sample mass around 5 g. Fig. 1 shows uranium hydride powder after synthesis in the furnace. Small amount of this powder (nearly 30 mg) was then prepared in pure argon inside the glove-box for XRD analysis. Powder was placed inside a specific and tight sample holder from Brucker under argon. So, the obtained powder could be

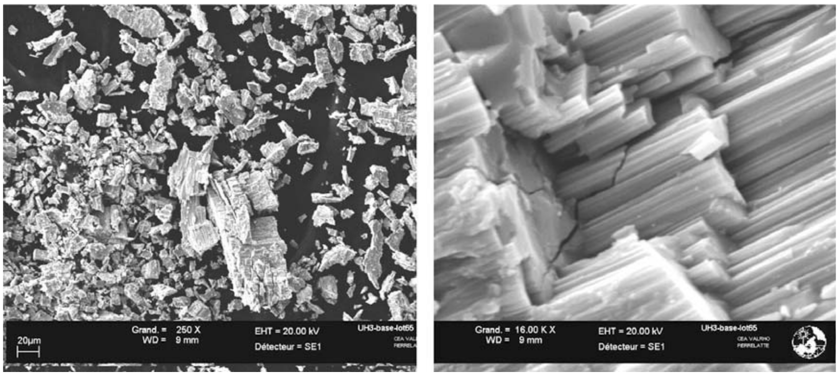

Fig. 2. Uranium hydride grains observed by scanning electron microscopy (X250 left and X16000 right).

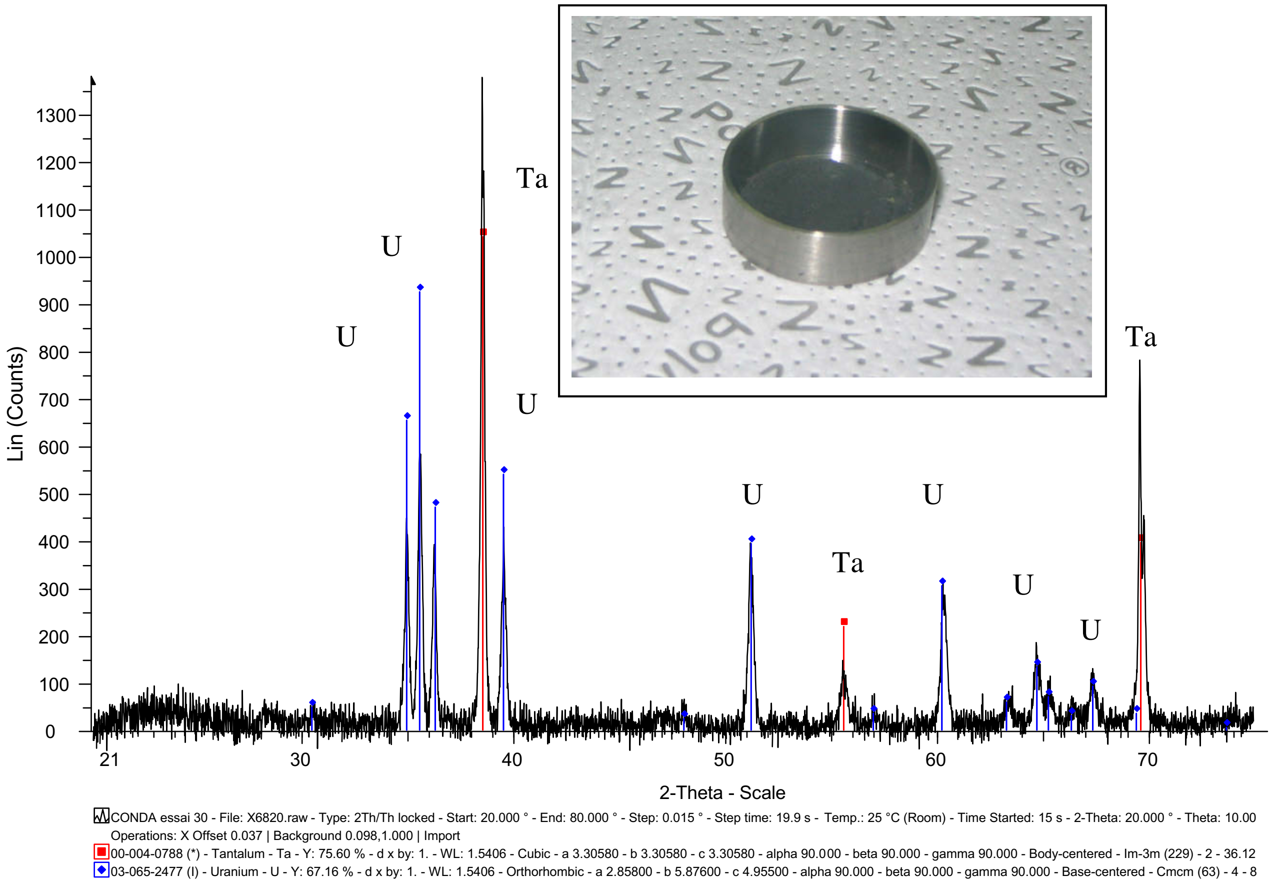

Fig. 3. Uranium fine powder after heat treatment in argon at 250 °C and XRD analysis.

analyzed in non-oxidizing atmosphere on a Brucker D8 XRD device allowing observation of the real formed phases. The resulting XRD pattern (Fig. 1) showed only uranium hydride peaks. Only very few uranium oxide UO_2, lower than 1 wt.%, was detected by Rietveld pattern fitting. Tantalum peaks appeared because small amount was added to the hydride powder to calibrate the pattern.

Furthermore, grain size measurements by scanning electron microscopy showed two grain sizes inside the UH_3 powder. Small randomly shaped grains (a few μm) could be observed (Fig. 2) as well as large tabular grains (10–50 μm). This last population of grains appears with elongated angular platelets, all oriented in the same direction and sharp ridges (Fig. 2).

3.2. Synthesis of pure uranium powder

Uranium hydride was transformed into fine grained pure uranium powder after dehydration by heat treatment in pure argon at 250 °C in the furnace. Sample mass was around 3 g. Powder was dark black and sometimes agglomerated into small amounts. Fig. 3 shows uranium powder inside the glove-box. Small amount of this powder was analyzed by XRD with the same tight sample holder as the uranium hydride before and with the same experimental protocol. Fig. 3 shows the XRD pattern with uranium peaks, no more hydride peaks and with very few UO_2 (lower than 1 wt.%).

Grain size was observed by SEM and showed aspects close to those of the uranium hydride. The U fine powder was constituted with small grains (a few μm) and large tabular ones (10–50 μm) as seen in Fig. 4. It shows oriented structure with a morphology of fine agglomerated platelets as already observed for the uranium hydride grains before decomposition.

3.3. Ignition of uranium hydride in air

The powder sample about 2.3 g was placed inside a cylindrical stainless steel 15 mm diameter crucible. The sample was a 5 mm thick powder bed containing two K-type thermocouples for continuous monitoring of sample temperature during heat-treatment and ignition. The ignition test was performed in flowing air at a rate of 10 L min^{-1}. Before air was introduced in the furnace chamber, the sample was exposed to flowing pure argon during 10 min at room temperature. After switching to air atmosphere, the powder sample was maintained at room temperature during five more minutes. Afterwards, the sample was subjected to heating at 5 °C min^{-1} up to 500 °C in air, temperature was maintained constant at 500 °C during 30 min and finally sample was cooled at 10 °C min^{-1} until room temperature. Final atmosphere was again pure argon.

For 2.3 g of pure, dry and fresh uranium hydride, ignition was observed shortly after air was introduced while sample was still at room temperature. It occurred with a flash of lightning above the sample bed for about 10 s immediately followed by the apparition of an orange flame at the sample surface. In the same moment, a pressure variation round 15 mb was registered inside the furnace chamber. After this first step of gaseous combustion, a second step followed recognized by a solid combustion at the surface of the powder bed, running from the center of the free sample interface to the outer boarder of the crucible, and furthermore to

Fig. 5. First step of ignition: flash of lightning above the sample surface.

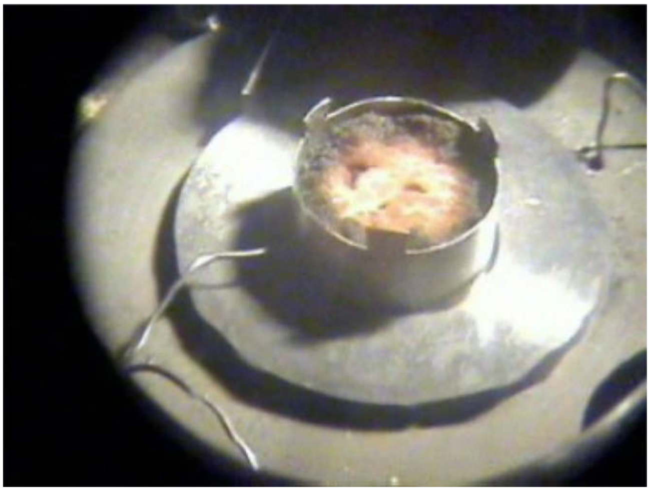

Fig. 6. Second step of ignition combustion in the solid phase.

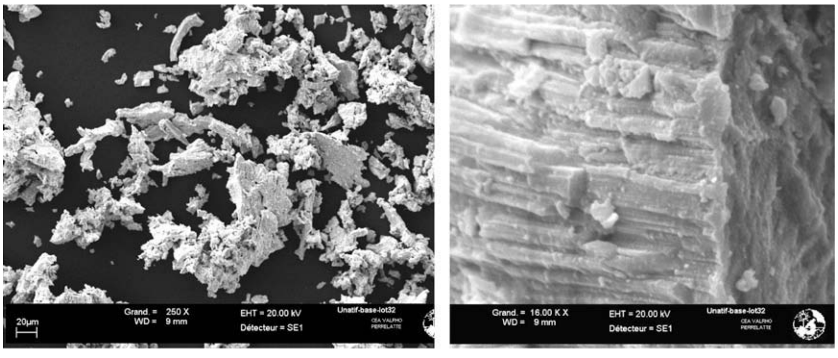

Fig. 4. Uranium grains observed by scanning electron microscopy (X250 left and X16000 right).

the bulk of the material. It must be noted that the volume of the powder bed significantly increased during ignition and during solid combustion, to reach finally two or three times the initial thickness after heating until 500 °C.

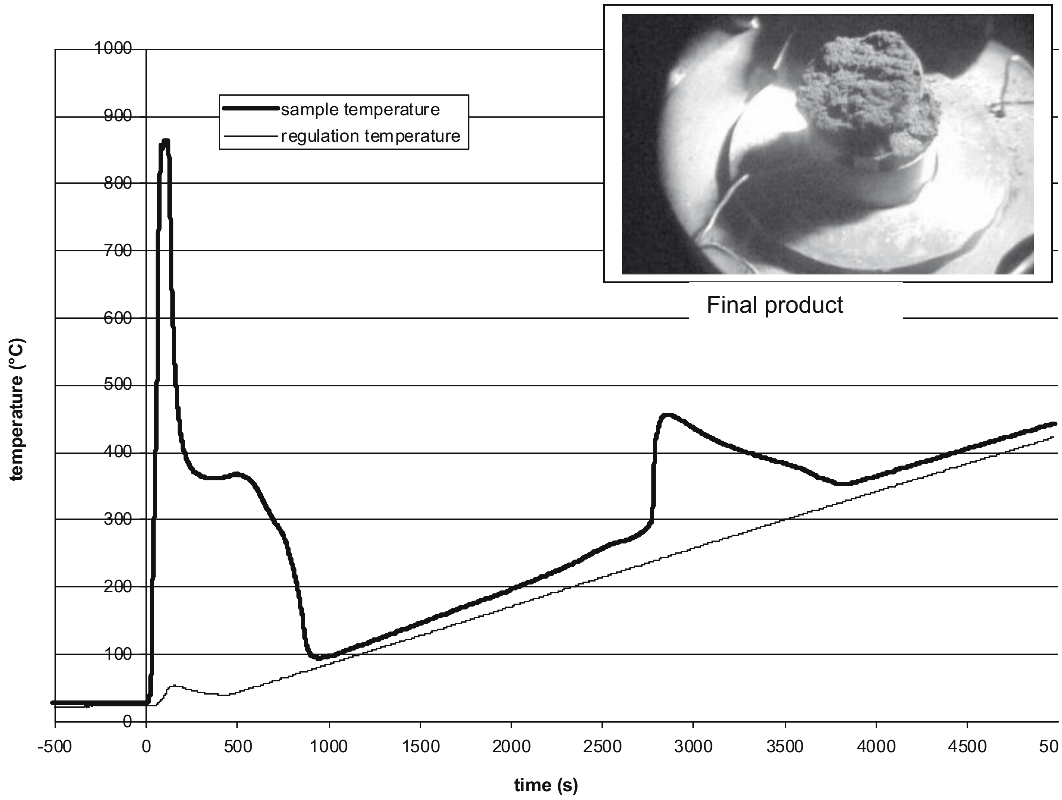

Fig. 7. Sample temperature measurement: temperature rise at ignition and during heating, volume increase after test in air.

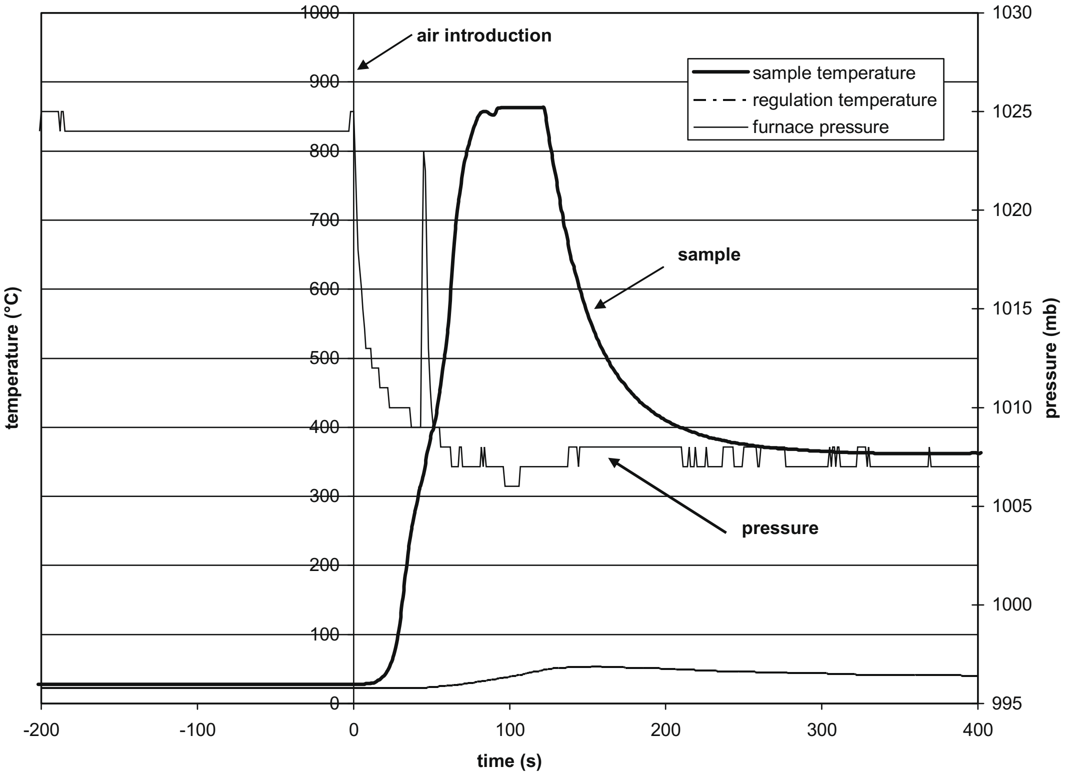

Fig. 8. Temperature peak at ignition and pressure variation inside the furnace.

Ignition corresponded to a brief temperature rise (the thermocouple placed inside the sample reached 863 °C) and temperature was still high (above 300 °C) during the solid combustion step during nearly 15 min. The first temperature peak occurred while sample was still at room temperature. After the solid combustion, uranium hydride is still present in the powder sample and uranium oxides UO_2 and U_3O_8 were formed, analyzed by XRD. The presence of U_3O_8 even at a low temperature of furnace regulation can be explained by the high temperature shortly reached during ignition (nearly 1000 °C). A second exothermic phenomenon, with lower intensity, occurred during heating, when the sample reached nearly 300 °C and can be attributed to final transformation into U_3O_8 oxide. The sample combustion is shown in Figs. 5 and 6. Temperature and pressure monitoring are presented in Fig. 7 (all the test) and Fig. 8 (focused on the first ignition step). XRD pattern of the reaction product just after ignition is shown in Fig. 9, volume increase and final product after heating until 500 °C in Fig. 7.

3.4. Ignition of uranium powder in air

In the same experimental conditions pure fresh and dry uranium powder was tested. A 5 mm thick powder bed with 2.8 g of uranium was exposed to air in the furnace, after 10 min under flowing pure argon. As well as in the case of uranium hydride, ignition occurred shortly after air introduction into the furnace, at room temperature. No flash of lightening was observed, only solid combustion occurred with uranium powder (Fig. 10). Sample temperature was still near 200 °C during several minutes. No significative pressure variation was noticed in the furnace during the ignition. Temperature and pressure monitoring are presented in Fig. 11. Final product was again U_3O_8.

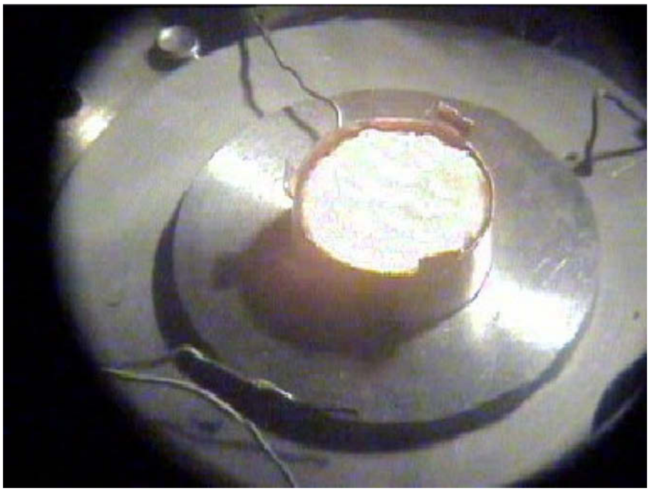

Fig. 10. Uranium powder ignition: combustion in the solid phase.

3.5. Characterization of final products

After ignition test and cooling to room temperature, XRD pattern showed only uranium oxide U_3O_8 (Fig. 12) both from UH_3 and U powder oxidized in air at 500 °C. The second temperature peak observed nearly 300 °C corresponded to complete transformation of the residual hydride or uranium and UO_2 into U_3O_8 oxide. U_3O_8 grains were observed by scanning electron microscopy. Grains obtained from UH_3 ignition are keeping the form of platelets with memory of the initial grain structure of the uranium hydride. Some smoothening appears at the surface of the elongated

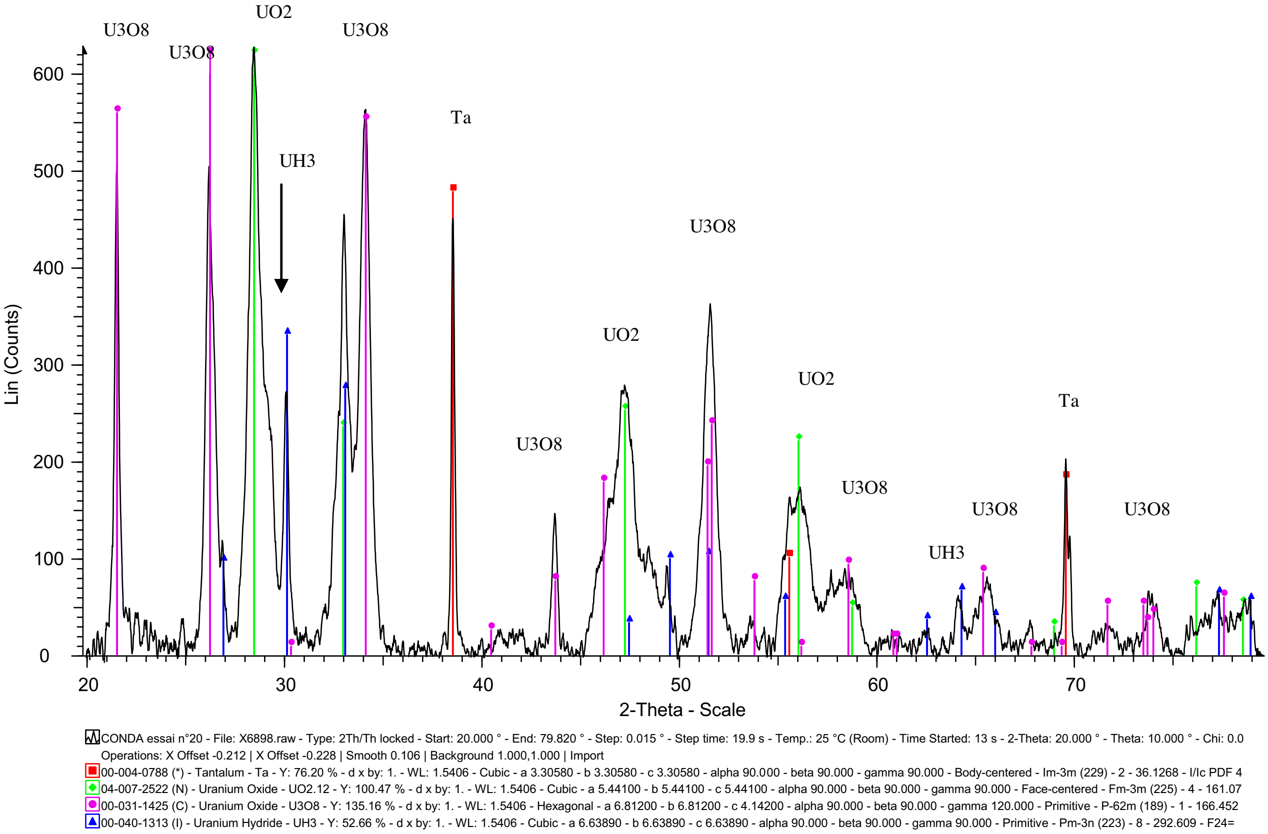

Fig. 9. XRD pattern just after ignition of UH_3 in air.

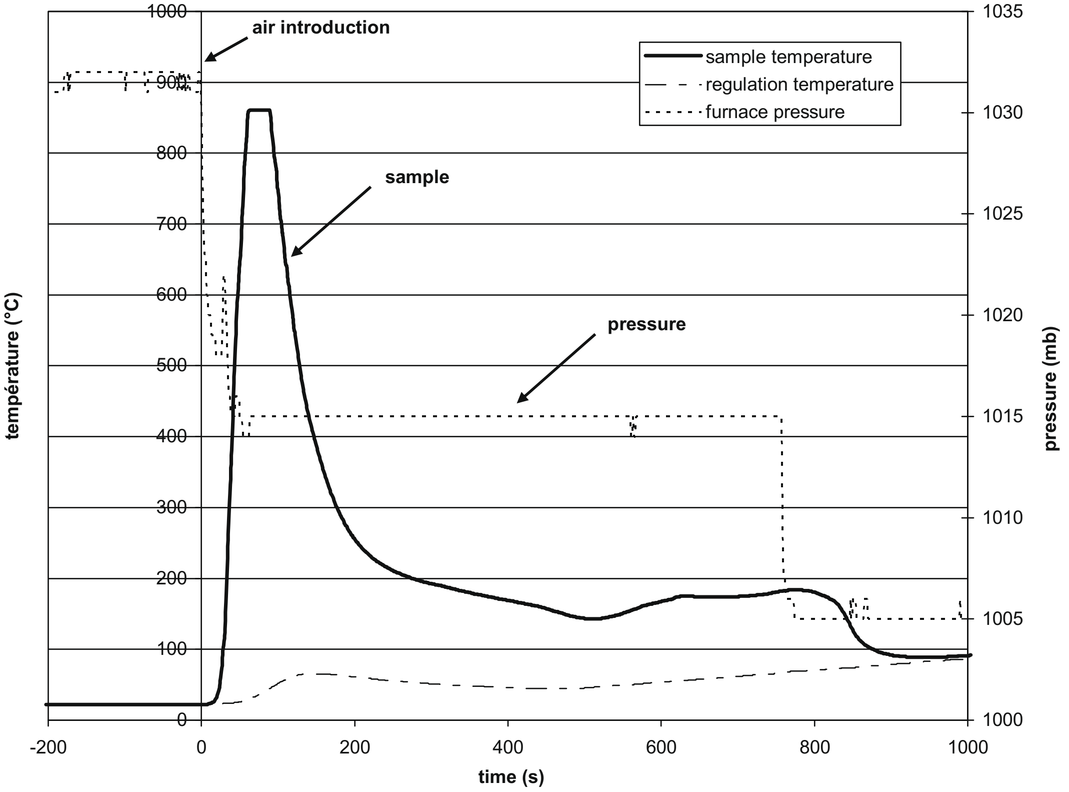

Fig. 11. Sample temperature measurement: temperature rise at ignition and during solid combustion.

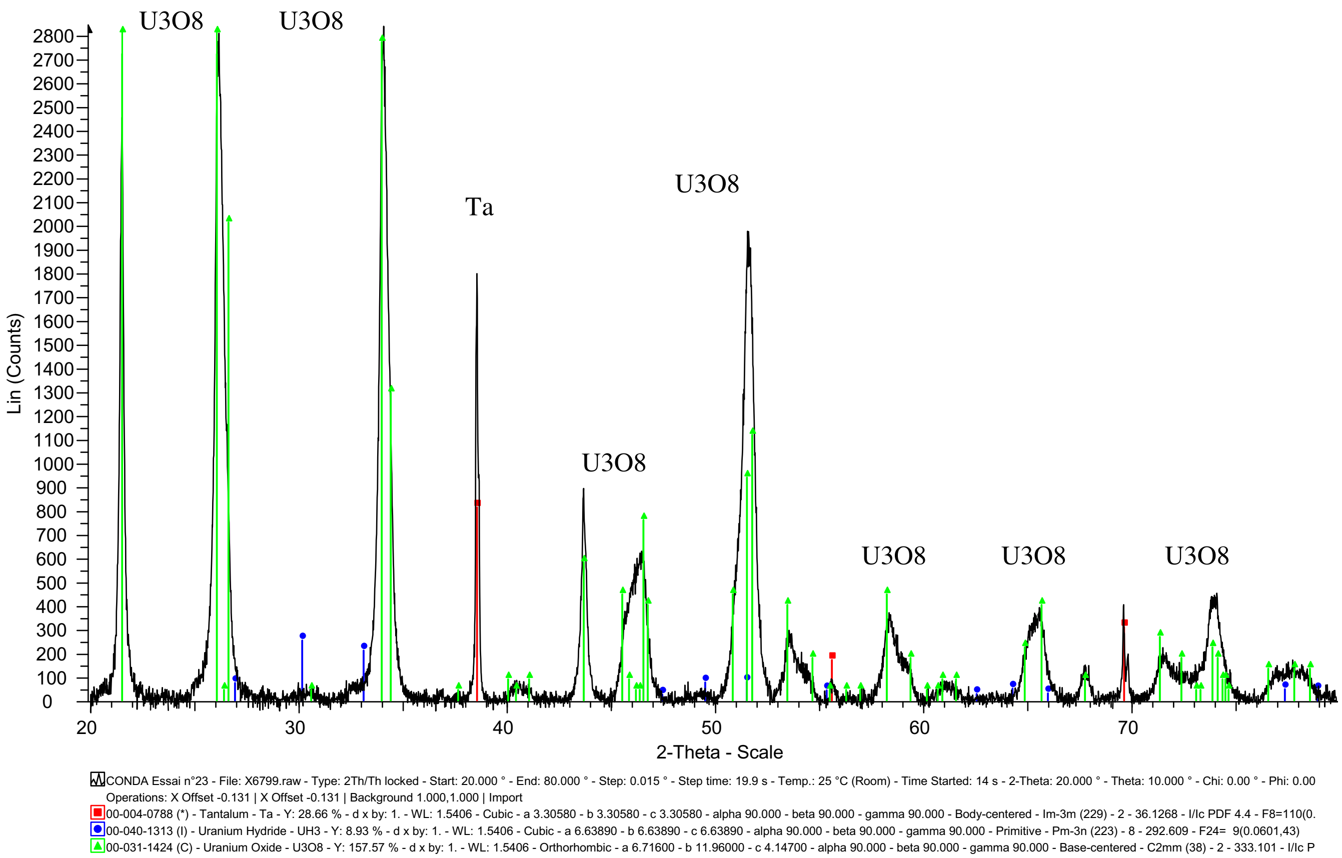

Fig. 12. XRD pattern after ignition of uranium in air: U_3O_8 oxide.

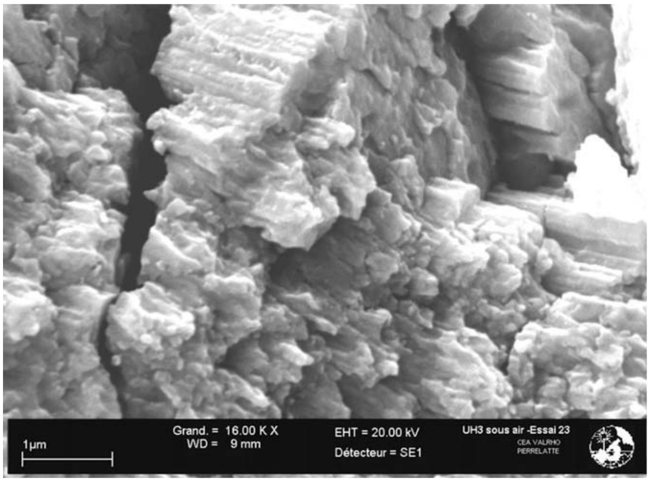

Fig. 13. Grains observed by scanning electron microscopy (X16000) after UH_3 ignition in air.

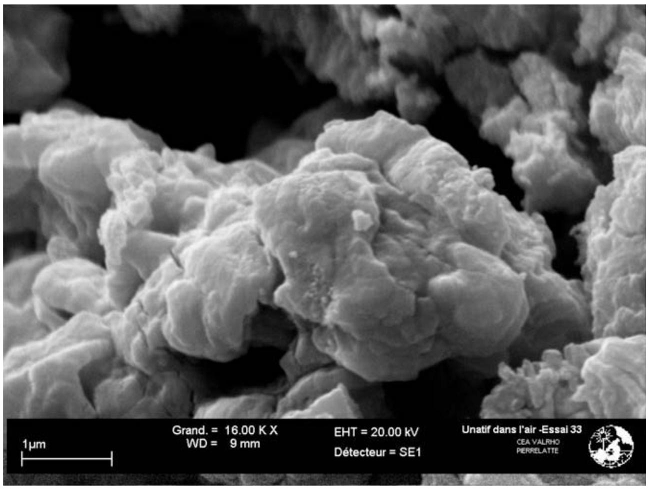

Fig. 14. Grains observed by scanning electron microscopy (X16000) after U ignition in air.

platelets and compared to the initial grains, ridges are less angular, grains are rounded up (Fig. 13). Grains obtained from U powder ignition are most of the time round grains with less memory of the initial platelets structure than in the case of UH_3 ignition (Fig. 14).

4. Interpretation

Experimental results about ignition in air of uranium hydride and uranium fine powders could be observed, monitored with a CCD camera and sample temperature could be registered continuously during ignition and heating. Ignition steps could clearly be identified.

Uranium hydride ignited through a two-step process including gaseous combustion with a brief flash of lightning and a flame at the sample surface in the beginning of the ignition, followed by a solid phase combustion step first at the surface and then inside the bulk of the powder bed during several minutes. Sample temperature rise until 860 °C and above was registered and during the solid combustion phase sample temperature was still maintained above 300 °C for several minutes. Ignition occurred at ambient temperature as soon as air was introduced inside the furnace.

For uranium powder bed in the same experimental oxidizing conditions, only the second step occurred: a solid phase combustion at the surface and inside the powder bed was observed. Again brief temperature rise was registered followed by several minutes near 200 °C and above, before sample temperature came back to furnace regulation temperature.

Oxidation of uranium hydride is strongly exothermic, with high reaction heat release:

$$UH_3 + 7/4O_2 \rightarrow UO_2 + 3/2H_2O, \quad \text{with } \Delta Hr = -1386\ \text{kJ mol}^{-1}$$

Uranium powder reaction in air is also highly exothermic:

$$U + O_2 \rightarrow UO_2, \quad \text{with } \Delta Hr = -1129\ \text{kJ mol}^{-1}$$

These reactions occur faster with small grain size. The high values of reaction heat explain the observed ignition phenomenon.

Based on these experimental results, following oxidation mechanism can be proposed:

- reaction with air of the small amount of uranium in equilibrium with uranium hydride present at the sample surface at the beginning of the test (partial oxidation),

  $$U + O_2 \rightarrow UO_2$$

- heat produced by this exothermic oxidation reaction induces dehydration of uranium hydride which can occur quantitatively in the powder sample,

  $$UH_3 \rightarrow U + 3/2H_2,$$

- hydrogen formation explains the combustion in the gaseous phase that was observed in the case of UH_3 in air, with a flame in presence of hydrogen and oxygen,
- oxidation in air of the uranium formed after decomposition of hydride (quantitative oxidation),

  $$U + O_2 \rightarrow UO_2,$$

- and finally, complete transformation follows: $UO_2 + 1/3O_2 \rightarrow 1/3U_3O_8$.

5. Conclusions

The UH_3 powder that was obtained in this study by heat treatment at low temperature in flowing $Ar/5\%H_2$ was very pure hydride as proved by XRD and Rietveld analysis. UH_3 grains were not surrounded with any small oxide layer which could protect the hydride, avoid further oxidation and prevent from ignition at low temperatures in air. This point can specially explain the ignition we observed at room temperature. Mass of the sample (a few grams) and the configuration of a powder bed well exposed to the flowing air can also explain this point. Oxygen could easily reach the powder.

Uranium fine and pure powders could be obtained by low temperature heat treatment in pure argon and short operating times. The PYRO test setup, with its low O_2 and H_2O amounts continuously controlled and maintained inside the glove-box, allows many applications concerning very reactive materials which must be protected from air. CEA continues to conduct active research on the pyrophoric behaviour of U-base materials, including materials for future nuclear cycle.

Spontaneous ignition was achieved at room temperature when uranium hydride or metallic uranium fine powders are freshly synthesized and kept away from oxygen and moisture.

Acknowledgement

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