Experimental report

22/12/2017

Proposal: 1-04-118 **Council:** 10/2016

Title: In situ study of the homogenization kinetics of a U-Mo alloy by neutron diffraction at high temperature

Research area: Materials

This proposal is a new proposal

Main proposer: Vincent KLOSEK

Experimental team: Vincent KLOSEK

Local contacts: Emmanuelle SUARD

Samples: U - Mo (7%) alloy

Instrument	Requested days	Allocated days	From	To
D20	4	3	27/01/2017	30/01/2017

Abstract:

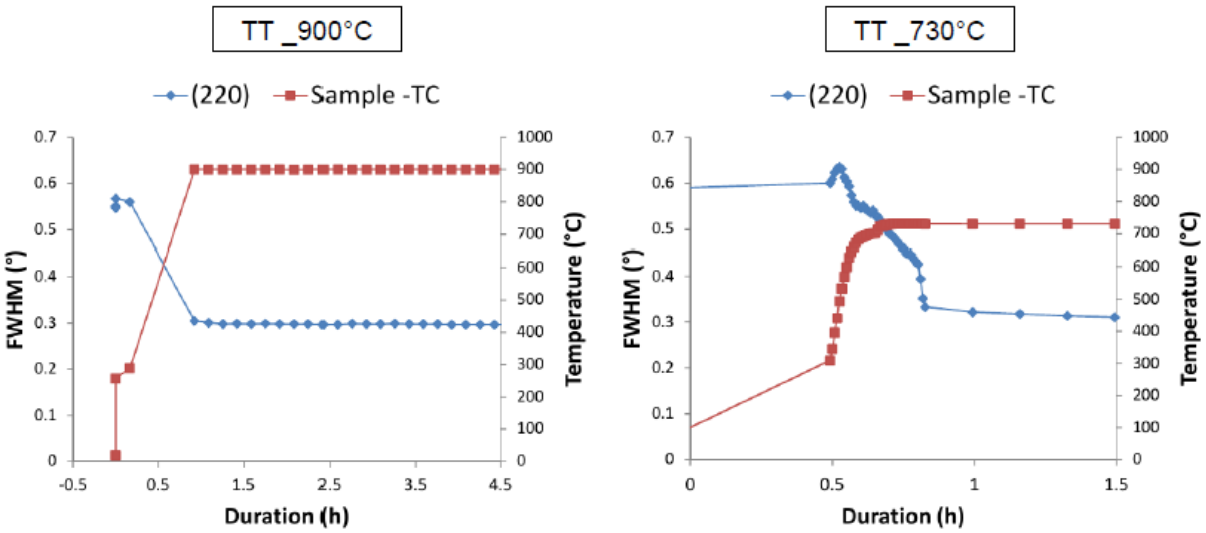
A worldwide program encourages the development of low enriched, high density U-Mo/Al dispersed fuel in order to convert research reactors cores currently working with highly enriched U3Si2 or UAlx fuel.In this high density U-Mo/Al fuel material, the fissile part usually consists of U-Mo spherical particles with diameter ranging from 20 up to about 150 µm, which are usually produced by an atomization process. During the solidification of the first solid phase in the molten metal, a U poor (i.e. Mo enriched) phase is first produced rejecting a U rich (Mo poor) liquid phase. High resolution neutron diffraction measurements have also confirmed the presence of volumes with different Mo contents as shown by the splitting of the gamma-U-Mo Bragg lines. The zones with low Mo content are strongly suspected to exhibit a higher swelling at low irradiation dose. The main goal of the proposed experiment is thus to characterize the Mo homogenization kinetics as a function of temperature by performing in situ neutron diffraction on U-Mo atomized powders during thermal treatments at 3 different temperatures (800°C, 900°C, 1000°C).

A worldwide program encourages the development of high density U-Mo/Al dispersed fuel in order to convert research reactors cores (Materials Testing Reactors, neutron sources…) currently working with U_3Si_2 or UAl_x fuel. This conversion has to fulfil requirements of nuclear non-proliferation treaty limiting the use of ^{235}U in nuclear fuels down to 20% in weight. In Europe, among several other reactors, the ILL, the FRM-II in Munich, the BR-2 in Mol (Belgium) and the future Jules Horowitz reactor (JHR) in Cadarache are now directly concerned by this commitment. In this high density U-Mo/Al fuel material, the fissile part usually consists of U-Mo spherical particles with diameter ranging from 20 up to about 150 µm (Fig. 1). These particles are usually produced by an atomization process. For the case of centrifugal atomisation, inside a high vacuum chamber, U-Mo droplets at high temperatures (about 200 °C above melting temperature, i.e., about 1400 °C) are poured onto a graphite rotating disk. Droplets are ejected and rapidly solidify. This rapid solidification is one of the main advantages of this manufacturing process: it helps retaining at room temperature the cubic high temperature γ phase of U (space group Im3m) which is metastable. Moreover many aspects of the microstructure of these particles are resulting from these ultra-fast cooling conditions. Metallographic inspections of as-atomized U-Mo particles show that they still exhibit the presence of dendrites. In particular elemental characterizations (EPMA, EDS or X-ray fluorescence) have shown that the center of U-Mo grains or cells is enriched in Mo whereas the outer part (i.e. closer to the boundary) is depleted in Mo (Fig. 2). The thickness of this zone close to grain boundary is evaluated to 0.3-0.6 µm. The presence of this Mo segregation in the grain (cell) core is a direct consequence of the large gap between liquidus and solidus which can be seen in U-Mo binary diagram. During the solidification of the first solid phase in the molten metal, a uranium poor (i.e. Mo enriched) phase is first produced rejecting a uranium rich (Mo poor) liquid phase. From a crystallographic point of view, it was shown very early on U-Mo ingots that for Mo concentrations of interest for this study, Mo is present inside the γ-U structure in U substitution [1]. On other words, γ-U-Mo is a solid solution: the γ-U-Mo cell parameter evolution with Mo content can be modelled by a simple linear relation. This has been confirmed later on atomised U-Mo particles using neutron and high energy X-ray diffraction [2][3]. High resolution neutron diffraction measurements have also confirmed the presence of volumes with different Mo contents as shown by the splitting of the γ-U-Mo Bragg lines. Finally, the most recent in-pile tests have revealed the necessity to use UMo particles with an optimised microstructure. Indeed the UMo zones with low Mo content are strongly suspected to exhibit a higher swelling at low fission density (irradiation dose).

During experiment n°1-04-118, performed in January 2017, Mo homogenization was first followed *in situ* using neutron diffraction on D20 high-intensity two-axis diffractometer. The diffraction patterns were recorded in the angular range $0.4° \leq 2\theta \leq 150.8°$ with the large one-dimensional position sensitive detector of D20. The wavelength was set to 1.54 Å by using a Ge (115) monochromator with a take-off angle $2\theta_m = 90°$, thus providing a good compromise between flux and resolution. Counting time was set to 10 min per diffractogram, excepting for the first homogenization heating for which the acquisitions were decreased to 30 seconds per diffractogram, due to the quite fast expected homogenization kinetics.

U-Mo powders were placed in cylindrical vanadium sample holders (~ 25 g of powder in each). Diffractograms were recorded *in situ* using a dedicated ILL-type resistive furnace under high vacuum. Two sets of atomized U-Mo7 powder were annealed under different conditions (4h at 900°C or 12h at 730°C), but up to comparable homogenization levels. Mo homogenization kinetics was thus

derived, following the evolution of FWHM of selected reflections as a function of the thermal treatment duration (Figure 1). It appeared that, in both cases, Mo homogenization was completed very quickly.



(a) (b)

Figure 1: Evolution of FWHM of γ-U-Mo 220 reflection and of sample temperature vs. time (preliminary results): (a) sample 1 (homogenization temperature of 900°C); (b) sample 2 (homogenization temperature of 730 °C.

At the end of these treatments, both homogenized U-Mo7 powders were tested at 450 °C i.e. to emulate fuel plate manufacturing conditions. Different kinetics for the destabilization of the γU-Mo7 phase and its decomposition into α-U and U_2Mo were observed (Figure 2), whereas both powders exhibit the same initial Mo homogenization level. Additional SEM characterizations explain this difference by a grain size effect, grains having grown much more in the sample homogenized at 900°C [4].

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

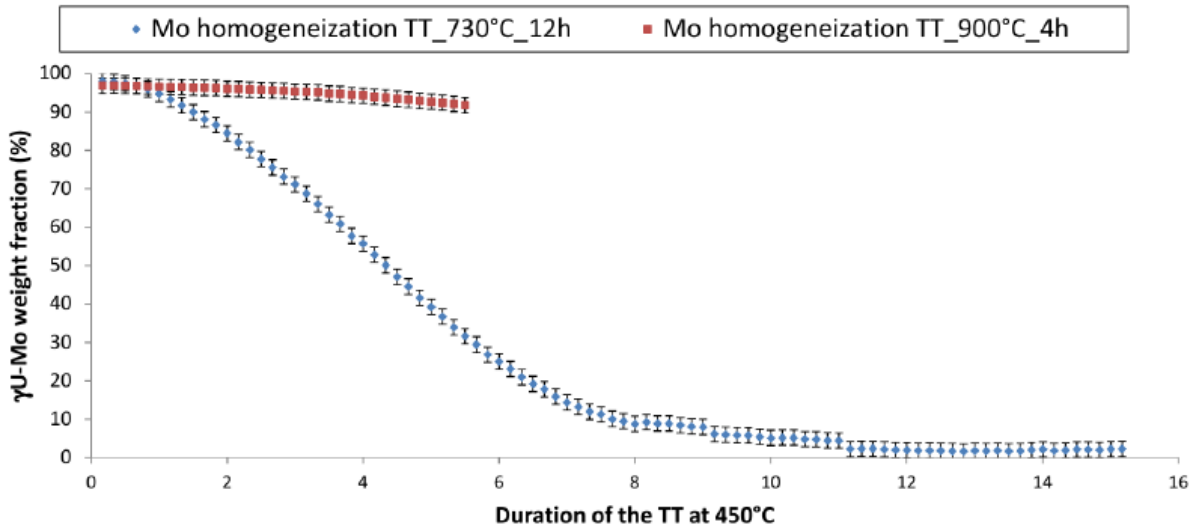


Figure 2: γ-U-Mo weight fractions deduced from Rietveld analysis of diffractograms as a function of time for both homogenized powders.

References

[1] A.E. Dwight, (1960) J. Nucl. Mater. 2, 81-87.

[2] J. M. Park, H.J. Ryu, K.H. Kim, D.B. Lee, *et al*., (2010) J. Nucl. Mater. 397, 27–30.

[3] A. Bonnin, J.P., Wright, R., Tucoulou, H., Palancher, Applied Physics Letters (2014) 105, 084103.

[4] H. Palancher *et al.*, RERTR Conference (2017).