Measuring the oxygen stoichiometry (O/M ratio) of nuclear fuels with thermogravimetry

INTRODUCTION

Most nuclear fuels are oxides of radioactive metals like uranium or plutonium, or blends of these. The oxygen-to-metal (O/M) ratio, or stoichiometry, is a critical parameter of nuclear fuel fabrication because it affects many of its properties. For instance, a too high O/M ratio may lead to a too low fuel's thermal conductivity, i.e. a less efficient heat transfer in the reactor.

Measuring the oxygen stoichiometry of nuclear fuels with thermogravimetry is a very accurate technique, based on measuring the subtle mass change from non-stoichiometric to stoichiometric composition at a given temperature and under a controlled oxidative or reductive atmosphere.

EXPERIMENT

- Samples: pellets of mixed uranium-thorium oxide made using different protocols:
  - o $(Th,3\%U)O_{2+x}$ sintered under oxidizing and reducing atmosphere
  - o $(Th,3.75\%U)O_{2+x}$ sintered under oxidizing and reducing atmosphere
- Instrument: Themys H2 TGA
- Temperature profile: heating from room temperature to 800°C
- Atmosphere: Ar + $8\%H_2$

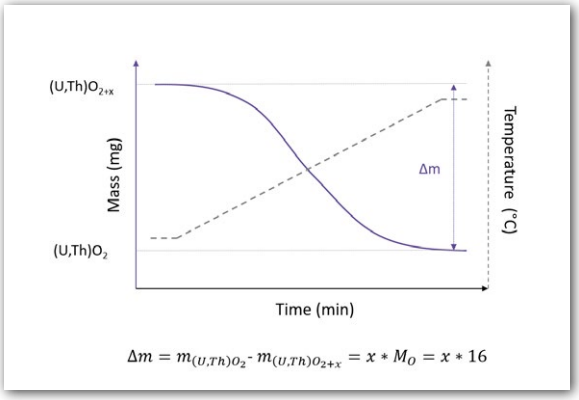

Figure 1 – Idealized mass change signal for the O/M ratio measurement, and calculation method.

RESULTS AND CONCLUSION

Under the final test conditions (Ar + $8\%H_2$ at 800 C), the dioxide is known to be stoichiometric, i.e. x=0. Using the mass loss recorded during the heating of the samples and applying the simple calculation shown on Figure 1, the O/M ratio of each sintered pellet could be measured.

The O/M ratio of pellets sintered in air was slightly higher than that of pellets sintered in reducing atmosphere. The authors attributed this effect to the interstitial oxygen introduced into the fluorite lattice of the mixed oxide structure during sintering in air.

Reference : P.M. Khot et al. / Journal of Nuclear Materials 420 (2012) 1–8.

Composition	O/M ratio	
	Oxidizing	Reducing
$(Th,3\%U)O_2$	2.008	2.00
$(Th,3.75\%U)O_2$	2.01	2.00

Table 1 – O/M ratio of the measured pellets

INSTRUMENT

THEMYS H2

ULTRA-HIGH TEMPERATURE CAPABILITY
to 1750°C with a single furnace

MULTIPLE BUILT-IN SAFETY SYSTEMS
for instrument and user's secured operations
• up to 100% Hydrogen capacity

HIGH ACCURACY & VERSATILE
hang-down symmetrical beam balance specifically designed for TGA applications

EXTERNAL COUPLING CAPABILITY
to 1000 °C with Mass Spectrometers

ACCURATE AND SENSITIVE
Tri- Couple DTA and DSC technologies up to 1000°C