

NUCLEAR MATERIALS CHARACTERIZATION



THERMAL ANALYSIS, CALORIMETRY & GAS SORPTION SOLUTIONS

- OXYGEN STOICHIOMETRY •
 - PHASE DIAGRAM •
 - IN-PILE BEHAVIOR •
- THERMAL STABILITY •

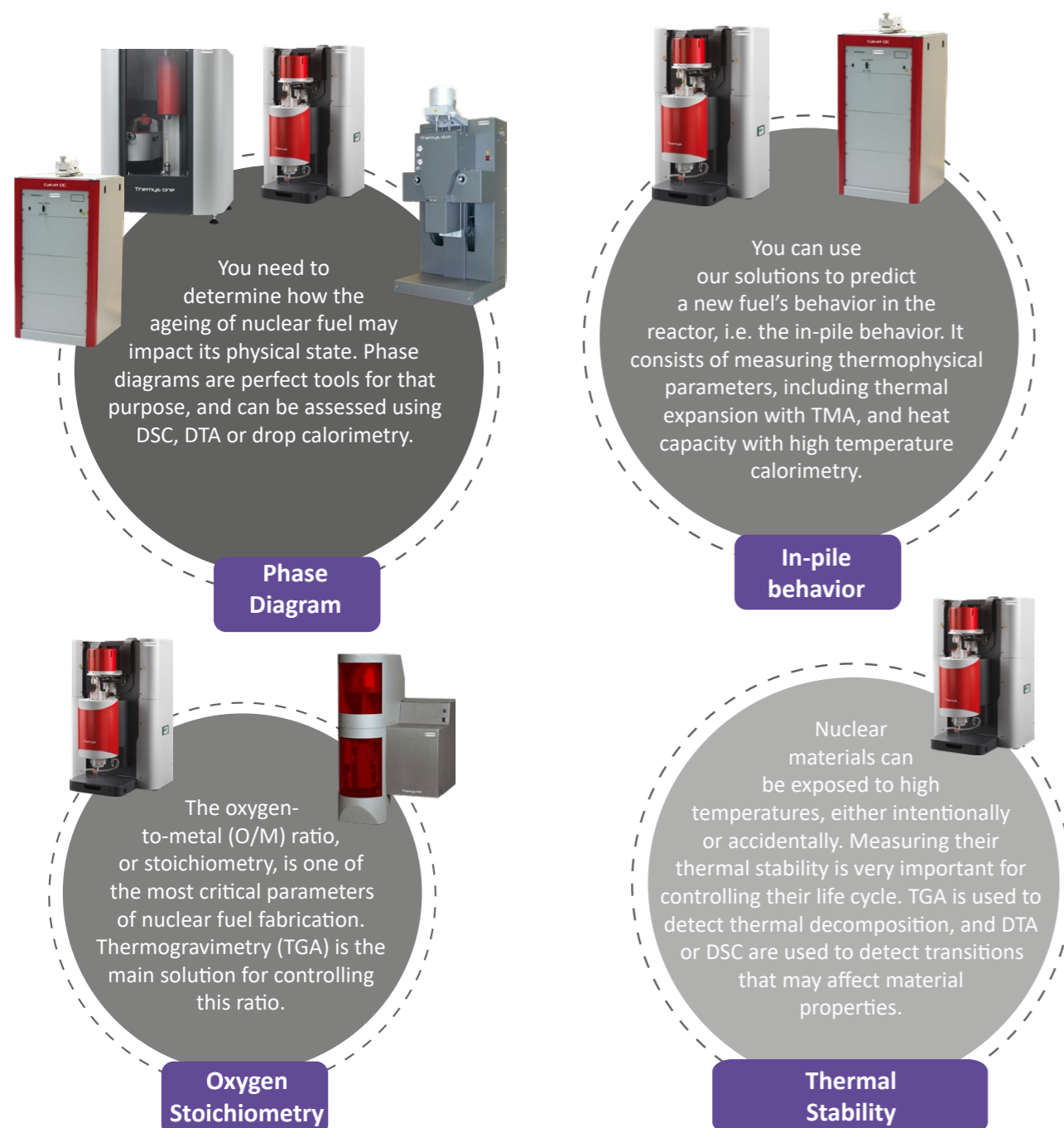
YOUR CHALLENGES

The nuclear industry is constantly searching for ways to improve. Optimizing the various processes employed along the nuclear fuel life cycle requires, among other things, research and characterization of new materials. Setaram offers solutions covering a broad spectrum of characterizations: thermal stability, thermophysical properties, composition of nuclear materials. These materials may be fuel, waste or any other non-radioactive material used in processes of varying temperatures and atmospheric conditions.

One challenge you may face with nuclear fuels and waste is that they need specific handling conditions. We can help adapt the relevant applications and solutions to fit in gloveboxes and hot cells.

COMMON CATALYSTS - STUDIES & SOLUTIONS

This brochure presents some of our solutions in this field and we encourage you to contact us for more information.



REIMAGINE MATERIAL CHARACTERIZATION

CUSTOMER TESTIMONIAL

"The calorimeter allows using of very small amount of studying materials with about 2 mg. Such, we can use this machine for study not only Th and U bearing materials but also Np and Pu containing phases. Using standard methods of calorimetry we can determinate enthalpy of formation of studied materials."

S. Neumeier et al, Material Science for Nuclear Waste Management, Energy & Environment Band, Volume 327, ISBN 978-3-95806-155-2

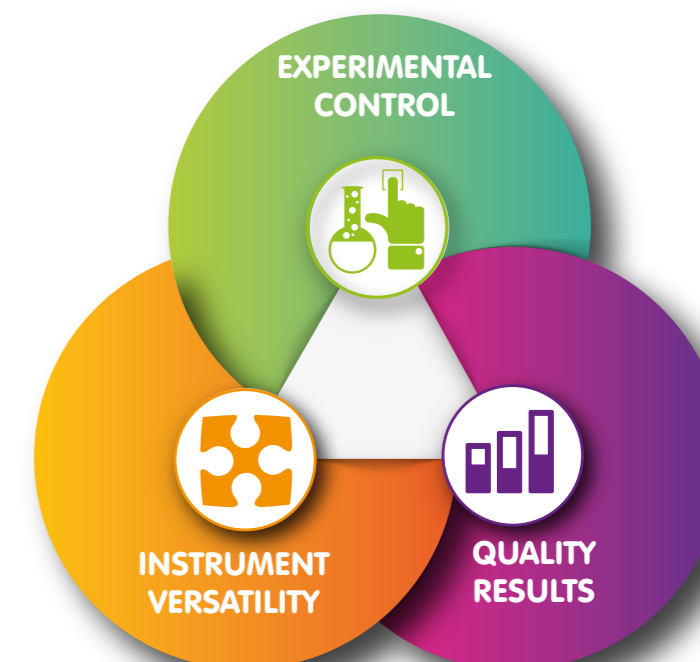
THE KEP TECHNOLOGIES ADVANTAGE

KEP Technologies is addressing its offerings to the nuclear market by making available the widest and most versatile choice of solutions. Now you can consult with one company, KEP Technologies, to address your challenges across the broadest number of battery studies on the market.

Each solution embodies our "Reimagine Material Characterization" value proposition by delivering the three core customer benefits of **Experimental Control, Instrument Versatility and Quality Results.**

We believe solutions that provide these benefits will deliver the highest value to our customers.

In addition to our core customer benefits, we are able to provide **customized solutions** by harnessing the engineering and project management of our highly skilled organization.




CUSTOMIZED SOLUTIONS

Modular design allows for upgraded and tailored functionality
Access to all previous non-proprietary custom requests
Open access to our engineering development team

REIMAGINE MATERIAL CHARACTERIZATION

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
- **VERY HIGH TEMPERATURE**
DTA technology up to 1750°C

SPECIFICATIONS

Temperature range (°C)	Ambient to 1 750
Programmable heating rate (°C/min)	0.01 to 100
Vacuum	< 5.10-2 mbar
Measuring range	+/- 20 mg +/- 200 mg
Resolution	0.002 µg 0.02µg

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

APPLICATION

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%H₂

RESULTS AND CONCLUSION

Under the final test conditions (Ar + 8%H₂ 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.

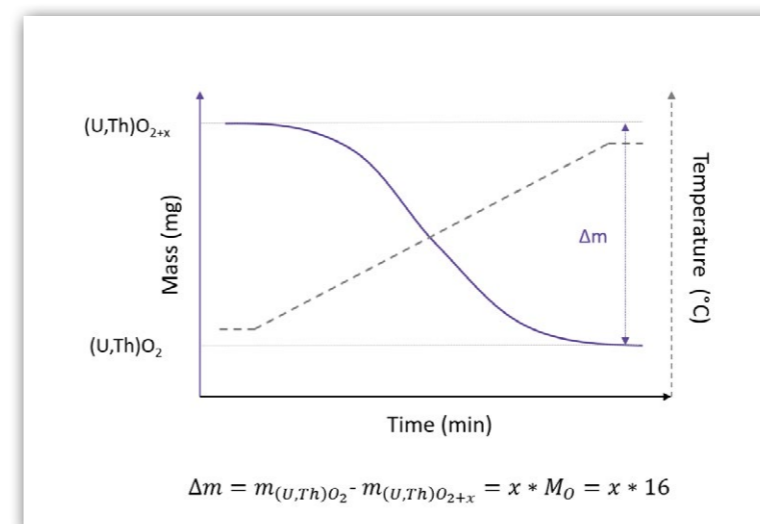


Figure 1 – Idealized mass change signal for the O/M ratio measurement, and calculation method.

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

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

INSTRUMENT

CALVET DC



IMPROVED HEAT CAPACITY AND HEAT MEASUREMENTS WITH THE CALVET DC

- heat flux DSC up to 1600°C – for accurate heat capacity, heat, and glass transition measurements
- drop calorimetry up to 1500°C – for accurate heat capacity, heat of dissolution and heat of formation measurements

VARIETY OF ATMOSPHERE CONDITIONS

possible with multiple carrier and reactive gas options

CONVENIENCE AND ECONOMY

with one instrument and furnace for TGA, TG-DSC, TGDTA, DSC, DTA, and TMA up to 1600°C

MODULAR ADAPTATION ALLOWING

TGA only, DTA only, TG-DTA up to 2000°C all in one instrument



SPECIFICATIONS

	CALVET DC	THEMYS LV
Temperature range (°C)	room temperature to 1600	
Isothermal and temperature scanning (°C/min)	up to 20	
Sample volume (μl)	up to 450 for heat flux DSC and 5700 for drop calorimetry	up to 18100 in TGA
Sample drop system	Manual or automated (optional)	

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

APPLICATION

Phase diagram of molten salts

INTRODUCTION

Molten Salts are believed to be a good solution to replace water as a heat transfer medium in nuclear reactors. Their potential use in 4th generation nuclear power plants has renewed interest of the nuclear science community since ORNL (USA) recently started again project kept dormant since the 1960s. This move forward was accelerated by the Fukushima accident in Japan, as the power failure of the cooling circuit pumps of the reactors, lead to extreme water temperature, hydrogen formation and its subsequent explosion.

It isn't likely to happen in a so called fluoride salt high temperature reactor (FHR) because the molten salts have extremely high boiling point and extremely low vapor pressure. Moreover, new concepts of reactors employing liquid uranium fluoride based fuels instead of solid fuel are under study. In case of loss of control of the reactor, it leads to a stop of the reaction, so a stop of the heat production. It is thus qualified as "inherently safe" reactors.

But it makes then clear that there is a need to study complex molten salts phase diagrams, conduct a lot of dissolution experiments and measure the heat capacity of all of these materials and blends of materials.

EXPERIMENT

Some labs have already started producing experimental thermodynamic databases like the Joint Research Center (Institute of Transuranium Elements) where CALVET DC with HF DSC and Drop sensor are used by Dr Ondrej BENES and his team. They worked on the thermodynamic properties of the LiF-ThF4 system potentially meant to be used together with 235U or 239Pu in the form of fluorides serving as startup fissile material [1].

RESULTS AND CONCLUSION

The enthalpy of mixing of the LiF-KF and LiF-ThF4 systems have been measured using an innovative temperature scanning method based on a CALVET DSC calorimeter and purposely designed closed cells including a nickel separator. CALVET DC is an isothermal or temperature scanning differential calorimeter with operating temperatures up to 1600°C and drop calorimetry capacities.

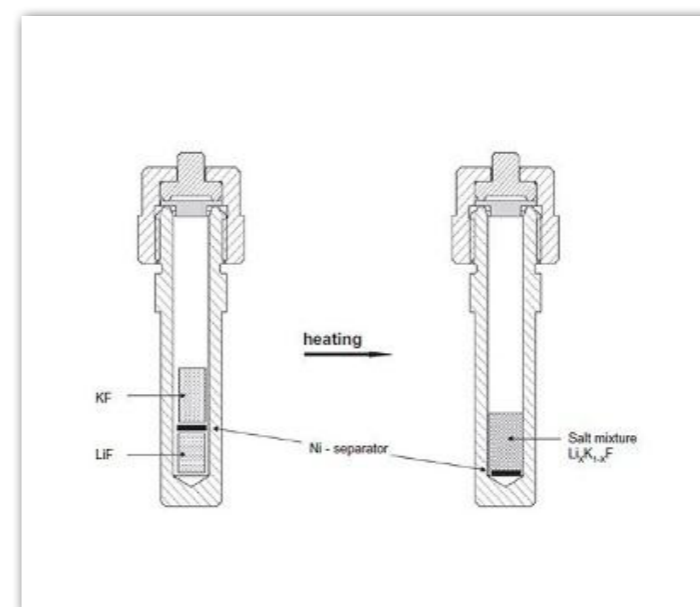


Figure 1 – special cell for determination of enthalpies of mixing involving a nickel based separator that melts before letting the two samples mix. From [1]

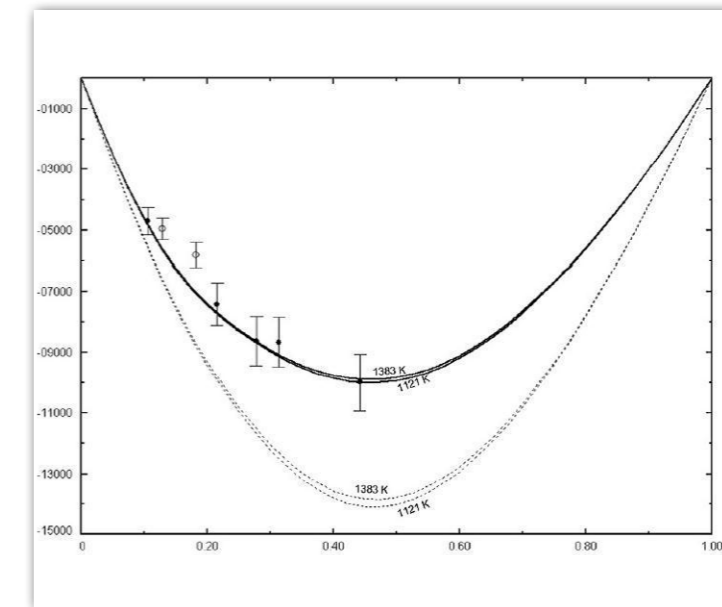
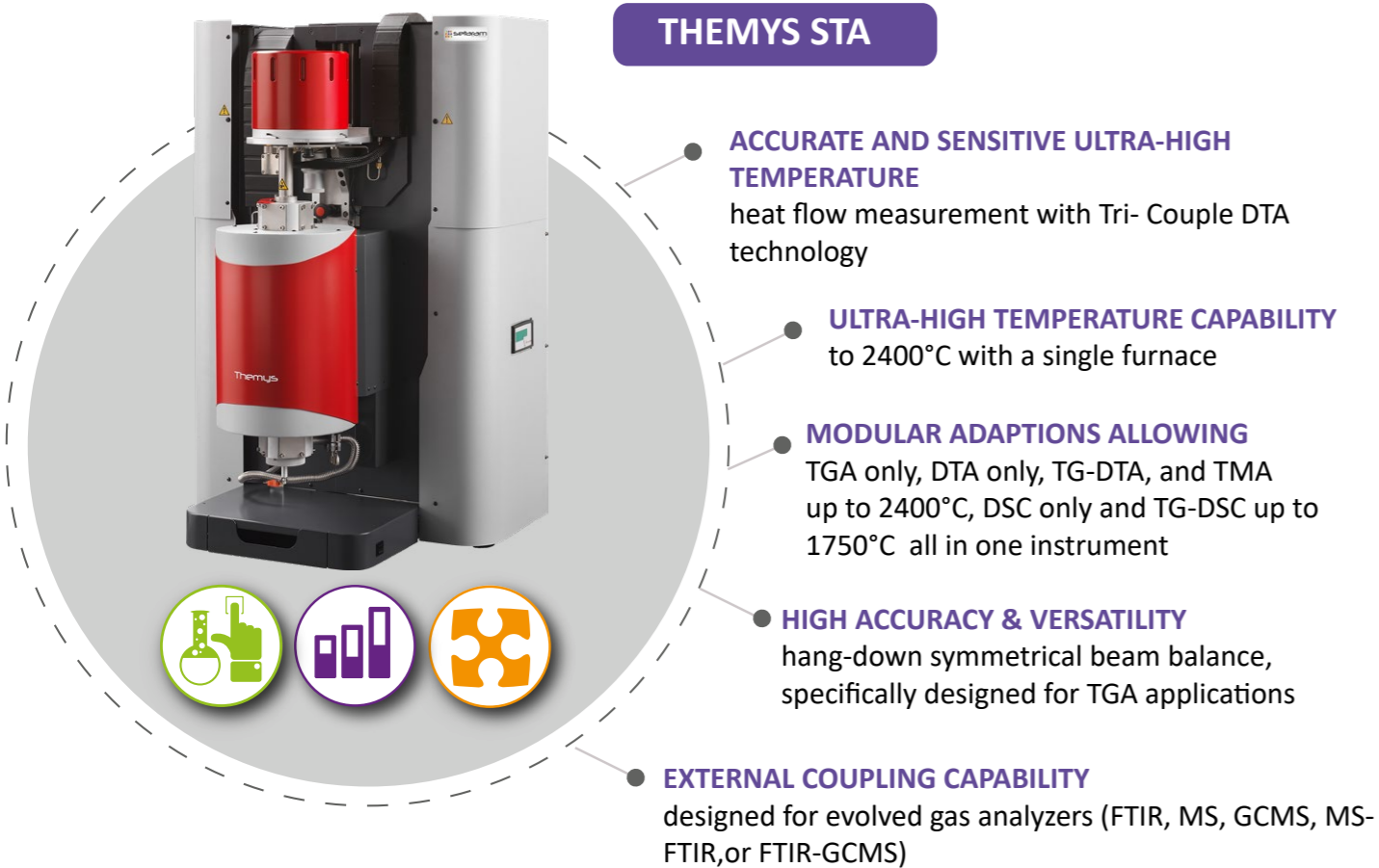


Figure 2 – Measured and simulated variations of enthalpies of mixing the LiF-ThF4 system. From [1]

Reference : E. Capelli et al. / J. Chem. Thermodynamics 58 (2013) 110–116

INSTRUMENT



THEMYS STA

- ACCURATE AND SENSITIVE ULTRA-HIGH TEMPERATURE**
heat flow measurement with Tri- Couple DTA technology
- ULTRA-HIGH TEMPERATURE CAPABILITY**
to 2400°C with a single furnace
- MODULAR ADAPPTIONS ALLOWING**
TGA only, DTA only, TG-DTA, and TMA up to 2400°C, DSC only and TG-DSC up to 1750°C all in one instrument
- HIGH ACCURACY & VERSATILITY**
hang-down symmetrical beam balance, specifically designed for TGA applications
- EXTERNAL COUPLING CAPABILITY**
designed for evolved gas analyzers (FTIR, MS, GCMS, MS-FTIR, or FTIR-GCMS)

SPECIFICATIONS

Temperature range (°C)	room temperature to 1750 or to 2400
Isothermal and temperature scanning (°C/min)	0.01 to 100
Sample volume (μl)	up to 2500 in TGA
Optional protected DTA rods for enhanced corrosion resistance, tricouple DTA rods for enhanced sensitivity, protected tricouple for combined advantages	

For more information on specifications please consult the product information and brochures available on our website : www.setaramsolutions.com

APPLICATION

Measuring phase transitions of a new candidate fuel material

INTRODUCTION

In a nuclear reactor, the initiation and control of a self-sustained nuclear fuel reaction (fission) take place. As the fission reaction progresses over time, various fission products emerge, leading to a change in the fuel's composition. Therefore, it is crucial to establish the phase diagram of the nuclear fuel in advance to assess the potential risk of phase transformation in the reactor caused by this compositional change. A phase diagram serves as a valuable tool for determining the temperatures at which phase transitions (such as melting, crystallization, and solid-solid transitions) occur in any candidate new fuel material, based on its composition. Hence, phase diagrams provide crucial insights into the potential risks of phase transformation within the reactor. High-temperature techniques such as DTA (differential thermal analysis), DSC (differential scanning calorimetry), or drop calorimetry directly measure the temperatures associated with these phase transitions in materials.

EXPERIMENT

- Sample: 200mg of U-15wt%UO₂ sintered cermet, a candidate fuel for fast reactor technologies.
- Instrument: THEMYS STA, with a tricouple DTA rod
- Crucible: alumina
- Temperature: from room temperature to 1200°C at 5K/min
- Atmosphere: argon flow at 2l/h

RESULTS AND CONCLUSION

As seen on Figure 1, the test helps determining three phase transitions over the tested temperature range:

- a solid-solid phase transition ($\alpha \rightarrow \beta$) at 940K
- a second solid-solid phase transition ($\beta \rightarrow \gamma$) at 1063K
- melting, or solidus at 1370K

As far as the cermet's application in fast reactors is concerned, the high solidus temperature of the candidate fuel provides a good margin between the reactor's operating temperature and the fuel's solidus.

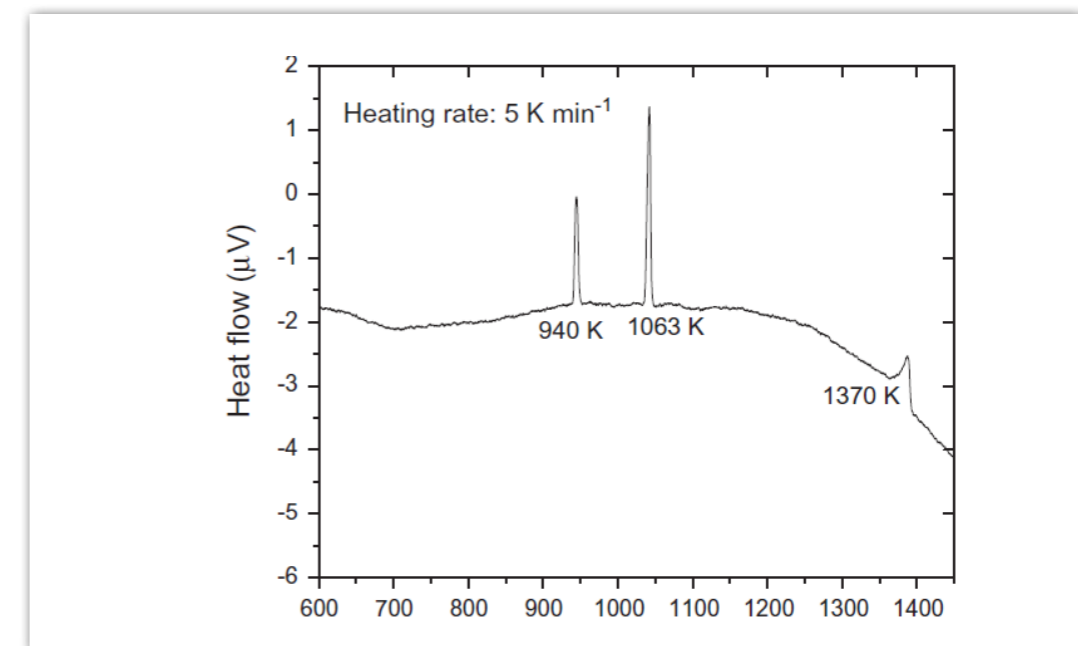



Figure 1 – DTA curve showing the peak corresponding to the detected phase transitions.

Reference : S. Mishra et al., Journal of Nuclear Materials 442 (2013) 400–407.

INSTRUMENT



THEMYS TMA

- PRESERVATION OF SAMPLES**
due to low load vertical TMA system
- ULTRA-HIGH TEMPERATURE CAPABILITY**
to 2400°C with a single furnace
- MODULAR ADAPPTIONS ALLOWING**
TGA only, DTA only, TG-DTA, and TMA up to 2400°C, DSC only and TG-DSC up to 1600°C all in one instrument
- ACCURATE AND SENSITIVE ULTRA-HIGH TEMPERATURE**
heat flow measurement with Tri- Couple DTA technology
- EXTERNAL COUPLING CAPABILITY**
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APPLICATION

Linear thermal expansion of (Pu_{0.25}Zr_{0.75})N pellets

INTRODUCTION

For the purpose of burning americium and degraded plutonium, implementation of accelerator driven systems (ADS) may enable a significant reduction of the radio-toxic inventories directed to geological repository. However, nitride fuels allow irradiation up to high burnup without degradation of safety margins or reprocessability. Therefore, in order to predict the in pile behaviour of nitride fuels, the thermophysical properties of plutonium-zirconium nitride (0-25at.% Pu), in particular the density, were measured on pellets.

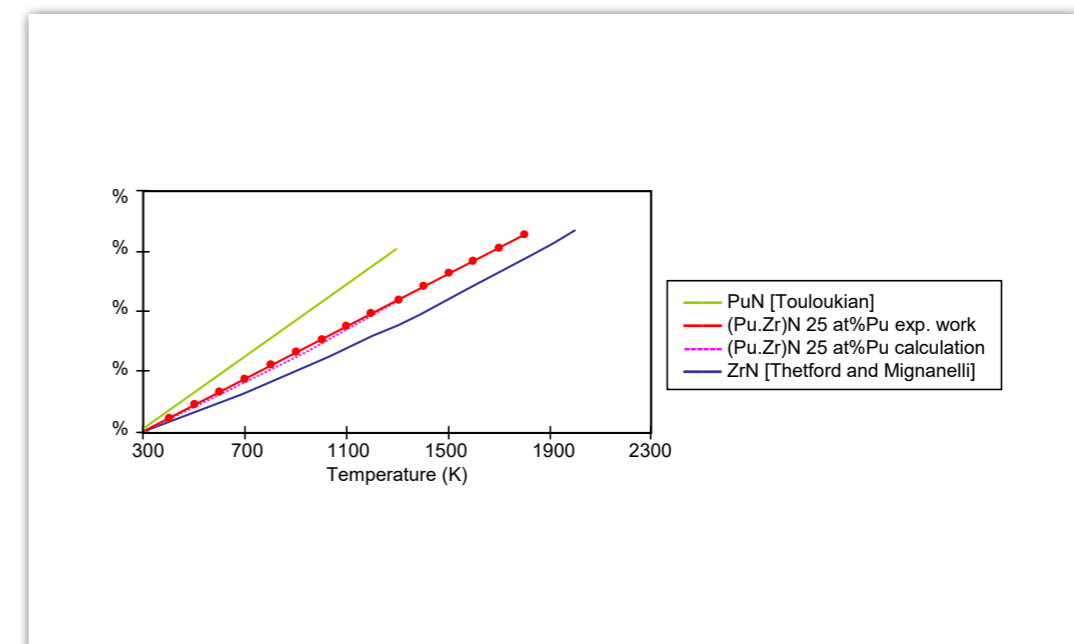
EXPERIMENT

To calculate the density with temperature, the linear thermal expansion coefficient data (Δ/L_0) can be determined experimentally from a THEMYS TMA. Then, density versus temperature can be calculated as $\rho = \rho_0 / (1 + \Delta/L_0)^3$ where the subscript 0 refer to the room temperature.


RESULTS AND CONCLUSION

The experimental results bring out that the variation of the thermal expansion of (Pu_{0.25}Zr_{0.75})N versus temperature was almost linear up to 1800 K, leading to a constant value of the linear thermal expansion coefficient of about $8.7-8.8 \cdot 10^{-6} K^{-1}$. Moreover, we can note that the measurements were in good agreement with the values calculated from PuN and ZrN available data according to the following mixing law:

$$\Delta L/L_0((Pu_x, Zr_{(1-x)})N) = v \cdot \Delta/L_0(PuN) + (1-v) \Delta L/L_0(ZrN)$$
 where v is the volume fraction of PuN in the solid solution.



INSTRUMENT



THEMYS STA

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heat flow measurement with Tri- Couple DTA technology
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APPLICATION

Thermal stability of nuclear materials under varying conditions

INTRODUCTION

Nuclear fuels are exposed to high temperatures and diverse atmospheres throughout their life cycle. These conditions can boost reactivity and accelerate aging. Thermogravimetric analysis (TGA) is used to determine the thermal stability of these materials. It detects mass variations linked to decomposition reactions, under realistic temperature and atmospheric conditions. Combined with Differential Thermal Analysis (DTA), it provides information on the heat released during these decompositions, and it can detect the phase transformations undergone by materials. The present example reports experiments carried out to test the pyrophoricity (fast reaction with air) of uranium hydride powders.

EXPERIMENT

- Sample: uranium hydride (UH₃) powder, 40 mg.
- Instrument: THEMYS TG-DTA.
- Temperature: heating from 30°C up to 500°C at 5°C/min.
- Atmosphere: air flow at 100ml/min.

RESULTS AND CONCLUSION

The TGA signal depicted in Figure 1 illustrates the sample's changes in mass and temperature over time. Upon initiating the heating process, a gradual increase in mass is observed. This indicates that the UH₃ sample exhibits a moderate reaction until it reaches temperatures ranging from approximately 140 to 160°C. At this point, ignition takes place, accompanied by a rapid increase in mass uptake. The DTA signal shown in Figure 2 confirms this observation by the presence of a distinct exothermic peak and a corresponding temperature rise.

After a few minutes, the samples' reactivity decreases. A small event is noticeable on the DTA curve, at about 200°C. A more intense final peak of reactivity occurs at about 300°C as seen on both TGA and DTA signals. This data set, together with extra measurements could help the authors concluding that the pyrophoric behavior of these powders could be mitigated with a pre-oxidation of the particles' surface.

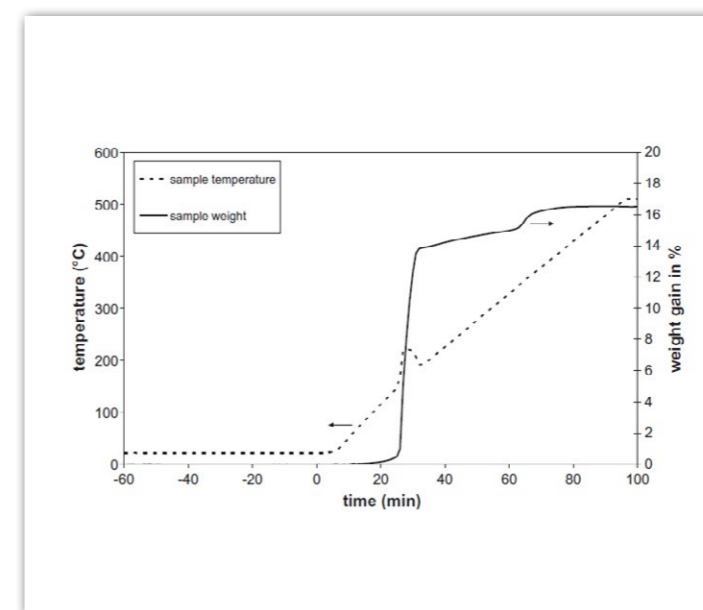


Figure 1 – TGA signal of the uranium hydride sample.

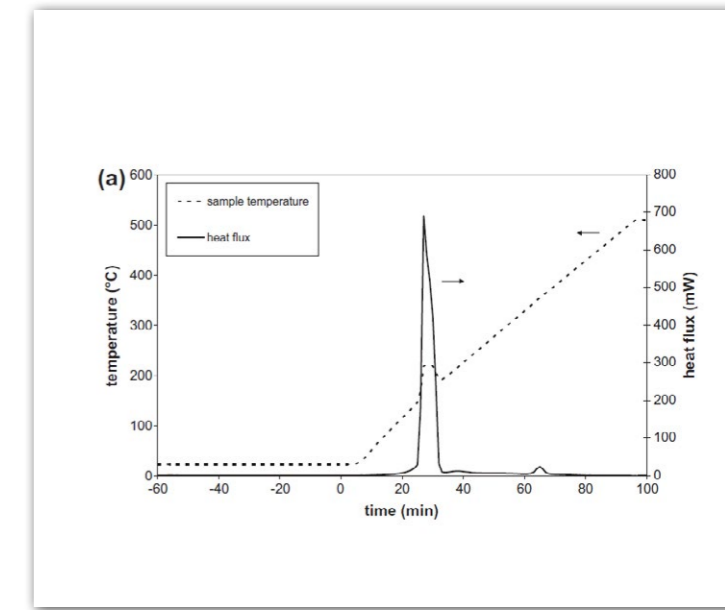


Figure 2 - DTA signal of the uranium hydride sample.

Reference : C. Ablitzer et al., Journal of Nuclear Materials 432 (2013) 135–145.

Adaptation of standard thermal analyzers and calorimeters to nuclear environments

CUSTOMIZED SOLUTIONS



REQUESTS ARE MULTIDISCIPLINARY & DIVERSE
about a hundred requests per year (international scope or special small-scale development)

NUCLEAR FIELD
with glove-boxing instruments for example, in the field of batteries, and for many applications under pressure.

PROCESS BASED ON EXPERTISE
we can either start from the standard instrument, from a database of a similar project, or we can start from 0 and deliver a turnkey solution.

OTHER EXAMPLES
we can design high pressure cells, a new rod, autonomous balances, crucibles with a specific material such as silver, new options for our instruments

Replicating the true conditions of material use (eg. under high pressure, or in corrosive, reducing or oxidative atmospheres), or working with environmental constraints (eg radioactive test materials) may require customized instrumentation. We manage special development projects in diverse environments and customize any instrument parameter including design, ergonomics, seismic resistance, sensors, operation range, electronics and software. The expertise of our R&D and Engineering teams make special developments a routine procedure for us.

Going further

There are applications outside the nuclear field for these customized instruments. Some examples include testing toxic materials, running tests involving flammable or explosive gases, or when contact with air may affect the integrity of the material being tested.

For more information on calorimetry for radioactive materials, please consult our Setsafe brand specialized in nuclear : www.setsafesolutions.com

INTRODUCTION

The study of radioactive materials requires handling of hazardous substances (fuels, wastes, reactive gases, etc.) under safe conditions for both the operators and the instruments that are used for characterization studies. In many cases, these materials need to be handled in glove boxes or in hot cells (lead chambers) depending on the radiation types and intensities.

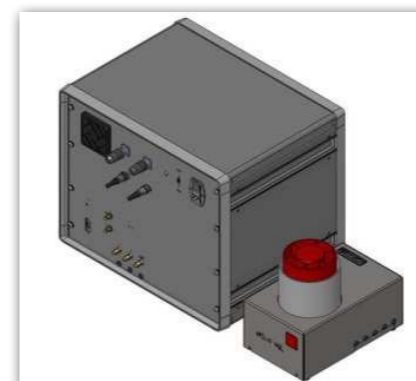
Thermal analysis and calorimetry are common thermal characterization techniques for nuclear fuels (current or candidates), wastes, and surrounding materials (ex: cladding). The instruments being used must be customized to be compatible with these specific operating conditions.

KEY ELEMENTS

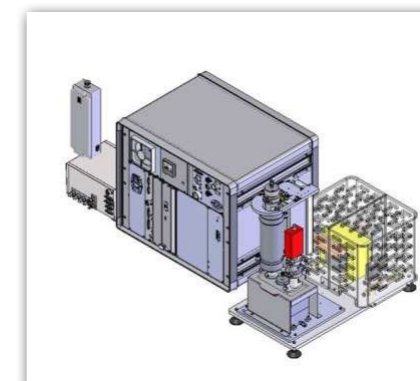
Setaram specializes in customized instrument design, has an expertise in electronics, and our R&D team is structured to be able to manage specific projects, which has allowed us to work in this field for a long time. One major issue is to separate the thermal analyser elements such as the furnace, the sample chamber and containers, the measuring modules, etc. which must be placed in a glove box or a hot cell, from the control and acquisition electronics. These are kept outside the glove box or hot cell because of their low resistance to irradiation and also to help with ease of maintenance of the instrument. Once designed and manufactured, the unit also needs to be installed by our qualified personnel, accredited to operate in nuclear environments.

TECHNICAL ACHIEVEMENTS

High temperature TGA, TG-DTA/DSC (for corrosion, stability, stoichiometry studies, long-duration isothermal reactivity of oxides), high temperature calorimeters (drop or heat flow methods for heat capacity and phase diagram determinations) or lower temperature calorimeters (for thermal activity of wastes, heats of reaction) have already been successfully customized to fit these specific conditions. See the pictures below.



Example of DSC : The electronic circuitry (left) is installed in a separate remote box to avoid its exposition to radiation.



"Customized" TGA to be placed in a glovebox



High temperature calorimeter placed in a glovebox (reproduced from E. Capelli et al. / J. Chem. Thermodynamics 58 (2013) 110 -116)



Switzerland – France – China – United States – India – Hong Kong
For contact details: www.setaramsolutions.com or setaram@kep-technologies.com

