In-situ experiments at elevated temperatures -an invaluable aid in studying MOX

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Introduction

In-situ experiments provide a unique opportunity to observe the behavior of materials as they change under the influence of external or internal factors such as temperature, pressure, chemical potential and thermodynamic equilibrium. This approach is of particular interest in the case of those oxides, for which the oxygen chemical potential varies strongly with composition. Mixed oxide nuclear fuels (MOX), such as $(U,Pu)O_2$, can be assigned to this group.

In-situ benefits

In all experiments on rare and hard to prepare materials, the aim is to obtain as much results as possible, while wasting the least amount of material. On the other hand, studies often demand the investigation of the properties as a function of composition, which in turn generates the need for preparing multiple samples, only slightly varying in the quantity of the constituting species. In principle, one could modify the composition of a given compound containing oxygen via oxidation or reduction processes, which in turn can be controlled by modifying the gas mixture around the sample at elevated temperatures.

Atmosphere control difficulties

In the extreme case of $(U,Pu)O_2$, the range of oxygen potentials of the gas required to obtain all the possible compositions (the area on the phase diagram between Pu_2O_3, UO_2, U_3O_8 and PuO_2 – oxygen to metal ratio $1,5<O/M<2,66$) is extremely wide. Also, the different phases present in this domain occupy very narrow intervals in terms of O/M, which invokes the necessity of exceptional precision in the measurement of the potential in the used gas and the ability to modify the value by small increments.

Experimental setup

Our main tool in this study was a state of the art X-ray diffractometer with a heating stage which allows reaching high temperatures up to 2000 K and fast change rates. It was equipped with an oxygen pump-gauge device based on an yttria-stabilized zirconia solid state electrolyte. We also installed a high efficiency moisture and oxygen filter to widen the available oxygen potential range. With this setup we were able to study, in-situ, a large part of the discussed domain, gaining unprecedented insight into the phenomena governing the changes that occur during thermal treatment. We were also able to investigate in detail the complicated structures of the different phases present in this domain.

Melting of MOX under air

We used our experience from these experiments to perform melting temperature measurements of our MOX samples under different atmospheres and establish a relation between this value and the O/M. We also performed various X-ray absorption measurements to gain further knowledge on the chemical properties and structure of the studied materials.

In-situ XAS

In May 2015 we carried out a series of in-situ high temperature XAS experiments on different mixed oxides using a specially designed setup at the ANKA synchrotron in Karlsruhe, Germany.

Conclusions, Perspectives

Coupled, these results should significantly enhance the knowledge base on the U-Pu-O system and the experience gained during the augmentation of the experimental setup can be easily translated to other equipment.