

Thermal analysis to understand reactional pathway of mixed oxalate decomposition

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Within the framework of the recycling of the valuable materials (actinides U, Pu) from irradiated nuclear fuel, the conversion is an important stage which is involved between both separation / purification processes and the steps of manufacturing of mixed fuel such as MOx. Thus this stage must be able to integrate purification flows while leading to oxides or mixtures of oxides adapted to the fuel shaping. These needs are even more marked with the deployment of the reactors of 4th generation and involve the development of new processes of conversion to take into account problems characteristic of this technological breakthrough (e.g. higher cadence, Pu content, liquid and gaseous effluents management, etc.).

To answer these future needs, new ways of synthesis were identified by the CEA, from the short-term adaptation of already existing ways based on the oxalic conversion, to more innovative ways requiring a longer-term R&D.

In this context, the way of oxalic co-conversion is investigated via the ANR ASTUTE project. The mixed oxalate obtained by precipitation undergoes a heat treatment to obtain mixed oxide. This heat treatment is then a key stage because it allows to control most of the morphological, textural and chemical final characteristics of the oxide. These characteristics are fundamental for the following stage which consists to the fuel manufacturing.

During this thermal conversion, a series of transformations take place before obtaining the final oxide. So as to predict and thus master the characteristics of this solid, a fine knowledge of the reactional scheme during the heat treatment is necessary.

The use of thermogravimetry in both controlled temperature program and isothermal conditions in the case of a uranium-cerium mixed oxalate allowed to isolate reactional intermediates during the conversion of the oxalate in oxide. These intermediates were characterized by chemical (IRTF spectroscopy), morphological (SEM) and textural (specific surface area and porous volume) point of view. By this way, a reaction scheme is proposed.

A deep knowledge of such a reaction scheme including the intermediate solids is essential to identify the key transformations and determine their kinetic behavior.