Special aspects of uranium oxide non-stoichiometry measurement by thermogravimetric analysis

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Abstract. Thermogravimetric analyses for determining uranium dioxide non-stoichiometry have been reviewed. Parameters of oxidation in air at various temperatures have been examined. The key parameters affecting accuracy of the obtained results have been evaluated. Oxidation parameters have been proposed, both for pure uranium dioxide as well as for uranium dioxide with added gadolinium oxide, which makes it possible to determine oxygen to metal (O/M) ratio with at least ±0.002 accuracy in weighed sample portions of approximately 3 g.

1. Introduction
Uranium dioxide is commonly used in modern nuclear reactors as nuclear fuel. Uranium-oxygen compound is one of the most complex systems. It comprises at least ten oxide phases, many of which have several polymorphic forms. For this reason it is important to study the phases occurring in UO₂ oxidation process as well as the effect of external conditions on their formation. This task becomes particularly difficult in case of fuel pellets with alloying additives, for example, burnable neutron absorbers. They are added to inhibit excess reactivity in nuclear reactors at the early fuel operation stage.

2. Materials and Experimental Methods
Oxygen to metal (O/M) ratio is an important parameter in the nuclear oxide fuel technology. This ratio has a direct bearing on chemical activity of fuel in relation to the cladding material as well as to the fission products resulting from nuclear fuel burnup. O/M ratio also has an effect on changes in physical properties, such as thermal conductivity, ductility, melting point, etc. Therefore O/M ratio determination in nuclear fuel is important for development and operation of modern nuclear power reactors.

Thermogravimetric analyses (TGA) are the most universal and accurate as they allow measurements to be performed in a wide non-stoichiometry range. Direct calculation and, consequently, no need of calibration are their undisputable advantages. Proper application of these analyses makes it possible to use small weighed sample portions in any condition – it may be an intact nuclear oxide fuel pellet or a sampled powder material.

Temperature dependence of uranium dioxide oxidation is characterised by a complex behaviour, because intermediate isothermal dwells and final temperature affect both the rate of oxidation as well as the length of incubation period. Dependence of oxidation kinetics on the rate of sample heat-up is low, however, as the heating rate increases incubation period is reported to shorten. The rate of
oxidation is highly dependent on sample density – dense samples are more resistant to oxidation, because they have a smaller open porosity and a poorer access of oxygen. Specific powder surface area and grain size also have a strong effect on oxidation of nuclear oxide fuel. The larger the area, the smaller the grain size, and the faster the process progresses. There is no clearly identified regularity of oxygen partial pressure’s effect on oxidation kinetics. In general, gadolinium and soluble additives stabilise fluorite phase which complicates oxidation process. This necessitates selection of optimal temperature parameters in order to study sample composition by TGA.

STA 409 CD (Netzsch, Germany) analyser equipped with Zirconia-M (OOO Issledovatelskiye Tekhnologii, Yekaterinburg) system for monitoring oxygen partial pressure in the furnace atmosphere was used for thermogravimetric studies of nuclear oxide fuel samples. The equipment with solid electrolyte galvanic cell was used to perform an independent evaluation of oxygen potentials as well as non-stoichiometry in the obtained samples. Uranium dioxide sample masses were determined by CPA225D (Sartorius, Germany) scales. JSM – 6610LV (JEOL, Japan) scanning electron microscope with wavelength range and energy-dispersive spectrometers as well as D8 Discover (Bruker, Germany) high-resolution diffractometer were used to analyse sample structures and phase compositions.

Uranium dioxide samples were manufactured using UO₂ powder fabricated by ADU process with the addition of 0.018 at.% aluminium in the form of Al(OH)₃. SEM image structure before sintering present in figure 1.

Figure 1. SEM image of the structure of ceramic UO₂ with 8% Gd₂O₃ before sintering.

Compacts were manufactured by the process of pressing compacts with the use of aqueous solution of polyvinyl alcohol as binder. Compacts were sintered in static Ar-8%H₂ atmosphere at temperature of 1350 °C for 8 hours. Final density of samples amounted to approximately 90 % of theoretical density (TD). X-ray phase analysis demonstrated the presence of only one phase on UO₂ basis. UO₂ lattice parameter was 547.11±0.04, which corresponds to stoichiometric composition. In addition, oxygen potential (at T = 1000 °C, which amounted to -447±3 kJ/mol) and O/M ratio = 2.0010±0.0005 were determined by means of the equipment with solid electrolyte galvanic cell.

It is common knowledge that UO₂ is oxidised to U₃O₈ in two stages, through forming of U₄O₉ or U₃O₇ oxides, depending on heat treatment parameters [1]. That is why first of all the measurements were performed by differential scanning calorimetry (DSC) combined with thermogravimetry (TG). Heat-up was carried out at the rate of 10 °C/min up to the temperature of 800 °C in the desiccated air with the flow rate of 50 ml/min. Two peaks were identified during oxidation, and the oxidation process terminated at 450 °C. Regarding the peaks, temperature values representing the beginning and the end of reaction were determined: they totalled at 248 and 290 °C for the first peak, and 379 and 394 °C – for the second.
Subsequently, samples were subjected to oxidation in a ceramic crucible made of BeO in the desiccated air with the flow rate of 50 ml/min. For measurement purposes pellets were fragmented to pieces of 1-2 mm, which ensures a larger extended surface contacting with the furnace atmosphere. Samples were heated at the rate of 10 °C/min. The temperature program included two isothermal dwells – at 1200 °C and 1000 °C. Sample mass equaled approximately 3 g. It has been identified that any changes in masses cease at 700 °C. The curve levels off before 900 °C, and with further heat-up to 1200 °C loss in mass is demonstrated. Uranium-oxygen phase diagram [2] implies that at temperatures exceeding 800 °C U3O8 already starts to noticeably deviate from its stoichiometric composition. Analysis of oxidised product diffraction patterns showed the presence of α-U3O8 phase and traces of β-U3O8. Consequently, loss in mass at high temperatures is related to changes in U3O8,9 equilibrium composition.

Therefore, oxidation conditions involving heat-up to 800 °C at the rate of 10 °C/min in the desiccated air with the flow rate of 50 ml/min were selected to determine O/M ratio. Initial O/M ratio in a sample based on oxidation pickup through to stoichiometric U3O8 was calculated as per ASTM C1453 [3].

The average O/M value for five measurements amounted to 2.0017±0.0003, which corresponds to the values obtained from X-ray analysis data and by means of the equipment with solid electrolyte galvanic cell. Subsequently, based on the obtained X-ray as well as TGA data, the temperature program for oxidation was modified by adding an intermediate isothermal dwell at 600 °C.

For the purposes of checking the proposed procedure the samples with over-stoichiometric composition were obtained both by specifying oxygen potential of furnace atmosphere as well as by controlled oxidation in air. O/M ratios for these samples, determined by means of the solid electrolyte galvanic cell technique stood at 2.010±0.003, 2.020±0.003, and 2.050±0.005. The following O/M ratios were obtained by TGA: 2.011±0.001, 2.019±0.001, and 2.054±0.001. Thus, a good agreement of results obtained by different methods was achieved, which indicates a sufficient efficiency of the procedure for over-stoichiometric samples of undoped uranium dioxide.

The samples with 8 wt.% Gd2O3 content were manufactured by the process using dry lubricant (binder) – aluminium stearate (estimated Al quantity amounts to 0.023 at.%). Sintering was performed in a dilatometer with dwell time of about 8 hours at maximum temperature of 1600 °C in Ar-8% H2 atmosphere. Final density stood at approximately 10.3±0.1 g/cm3 (96% TD). SEM image structure after sintering is present in figure 2.

![Figure 2. SEM image of the structure of ceramic UO2 with 8% Gd2O3 after sintering.](image)

The conducted X-ray analysis showed that only one (U1,yGd)xO2x+y phase was present, with lattice parameter of 545.97±0.04 pm.

The papers dedicated to studying oxidation of uranium dioxide doped with rare earth metals [4-6] report an increased stability of fluorite-type structure as compared to U3O8 (at alloying element...
concentration of 4 to 10 wt.%) It is shown in papers [7, 8] that when performing oxidation at temperatures exceeding 350 °C in air an unstable (U,Gd)O₈ phase may be obtained. Within 350-450 °C range samples may demonstrate the presence of U₂O₈, U₃O₈ phases as well as a strongly over-stoichiometric UO₂ₓ with Gd dissolved in them, and at temperature of 450 °C and higher only a solid gadolinium solution is observed in U₃O₈. According to data provided in [7, 9], at temperatures exceeding 950 °C phases get separated into pure U₂O₈ and (U,Gd)O₈.

Measurements according to the temperature program involving heat-up to 1200 °C at the rate of 10 °C/min were performed to study oxidation kinetics in detail. Intense increase in mass already ceases at 590 °C, concurrently, the change in the rate of oxidation is observed at around 450 °C. Then the mass continues to slightly grow up to 856 °C, after which it starts to decrease through to 1200 °C. Loss in mass appears to be related to the separation of (U₁₋ₓ,Gdx)O₈ solid solution. It is of interest to note that ASTM C968 [10] recommends the maximum oxidation temperature of 900 °C, which is close enough to the temperature corresponding to the start of loss in mass. Therefore the primary task when selecting oxidation conditions for samples with gadolinium is to ensure the final composition of (U,Gd)O₈, because O/M ratio is calculated as per [10] exactly according to this assumption.

Further experiments conducted in combination with X-ray phase analysis of oxidation products showed that optimal conditions involve heat-up to 475 °C at the rate of 20 °C/min, dwell time of 4 hours, and cooling together with the furnace. After this the only phase present in the final product is (U,Gd)O₈. Initial O/M ratio in (U₁₋ₓ,Gdx)O₂ₓ samples is substoichiometric and stands at 1.988±0.002, which conforms to the sintering conditions in hydrogen-containing atmospheres. The main contributing components of the error in determining O/M ratio in this case are the selection of the required mass of the weighed sample portion for accurate pickup determination as well as the selection of oxidation conditions that would ensure that (U₁₋ₓ,Gdx)O₈ of stoichiometric composition is obtained as final product.

3. Conclusions

Temperature programs have been proposed to perform thermogravimetric measurements of non-stoichiometry in the samples of pure uranium dioxide or uranium dioxide doped with gadolinium. For the pure uranium dioxide the best results was obtained after heat-up to 800 °C at the rate of 10 °C/min in the desiccated air with the flow rate of 50 ml/min with an intermediate isothermal dwell at 600 °C. For (U,Gd)O₂ samples optimal conditions is a heat-up to 475 °C at the rate of 20 °C/min, dwell time of 4 hours, and cooling together with the furnace. The obtained parameters have been checked on samples with the known oxygen content measured by other methods. Accuracy and reproducibility of obtained data have been shown as good. The error of the selected O/M ratio measurement conditions does not exceed ±0.002.

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