Thermal properties of nonstoichiometry uranium dioxide

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Abstract. In this paper, was developed a method of oxidation pure uranium dioxide to a predetermined deviation from the stoichiometry. Oxidation was carried out using the thermogravimetric method on NETZSCH STA 409 CD with a solid electrolyte galvanic cell for controlling the oxygen potential of the environment. 4 samples uranium oxide were obtained with a different ratio of oxygen-to-metal: O / U = 2.002, O / U = 2.005, O / U = 2.015, O / U = 2.033. For the obtained samples were determined basic thermal characteristics of the heat capacity, thermal diffusivity, thermal conductivity. The error of heat capacity determination is equal to 5%. Thermal diffusivity and thermal conductivity of the samples decreased with increasing deviation from stoichiometry. For the sample with O / M = 2.033, difference of both values with those of stoichiometric uranium dioxide is close to 50%.

1. Introduction

The ratio of oxygen-to-metal (O / U) is the most important parameter of the oxide fuel, which determines the behavior of the fuel in the reactor core. Deviation from the stoichiometric composition (x = O / U - 2) influences on the basic properties of the fuel such as thermal diffusivity, thermal conductivity, ductility, melting point, diffusion coefficient, chemical interaction with the cladding and, as a consequence, the final fuel burning. Thus, the existence of preparation procedure of oxide fuel samples with different deviation from stoichiometry is important for the development and improvement of modern fuel nuclear power reactors.

The standard tablet without central hole was sintered in Ar-atmosphere with 8 % H_2 at 1600 °C for 8 hours. After sintering, the tablet was cut into several samples with the form of discs. Characteristics of the resulting samples are shown in table 1. The density of the samples was measured by hydrostatic method.

Table 1. Density of the samples.

№ sample	Density of sample (g/cm^3)	Mass (g)	Thickness (mm)	Diameter (mm)
1	10.346	0.97854	1.7332	8.411
2	10.339	0.97991	1.7372	8.418
3	10.340	0.98064	1.7378	8.412

2. Preparation of samples with given deviation from stoichiometry

Changing the oxygen-to-metal ratio of uranium dioxide samples was carried out on the NETZSCH STA 409 CD by thermogravimetry method. To control and change the oxygen potential of the gas flowing through the plant was used system, consisting of the oxygen sensor and the oxygen pump. The sensor measures the oxygen potential of the gas blown through the sample, and the pump is able to pump in or pump out oxygen from purging gas.

After sample preparation, was determined the initial deviation from the stoichiometry by solid electrolyte galvanic cell method (O / M = 2.002).

Using expressions (1) and (2) was calculated final weight of the sample that needs to be obtained by the sample oxidation to obtain the desired O / U [1].

$$\frac{O}{U} = \frac{(100 - U_S - Z - m)A}{15.999 \cdot U_S} \quad , \tag{1}$$

where U - the proportion of uranium in the sample, at. %; O - the proportion of oxygen in the sample, at. %; U_S - the proportion of uranium in the sample, wt. %; Z - total numbers of non-volatile impurities, wt%; m - moisture content and volatile impurities, wt. %; A - average atomic weight of uranium isotope mixture; 15,999 - the atomic weight of oxygen.

The atomic weight of isotope mixture calculated as:

$$A = \sum F_i A_i , \tag{2}$$

where F_i - mass fraction of the i-th isotope of uranium, A_i - the atomic weight of the i-th isotope of uranium.

The sample was placed on the Al_2O_3 sample holder and heated to 1300 ° C in a stream of helium. Then oxygen pump begins to add oxygen into helium to increase his oxygen potential until the sample mass comes up to the previously calculated. After cooling, the weight of the obtained sample were refined on the scales with an accuracy ± 4 mg and using the expressions (1) and (2) sample deviation from stoichiometry was received. A typical thermogravimetric curve of sample oxidation is shown in figure 1.

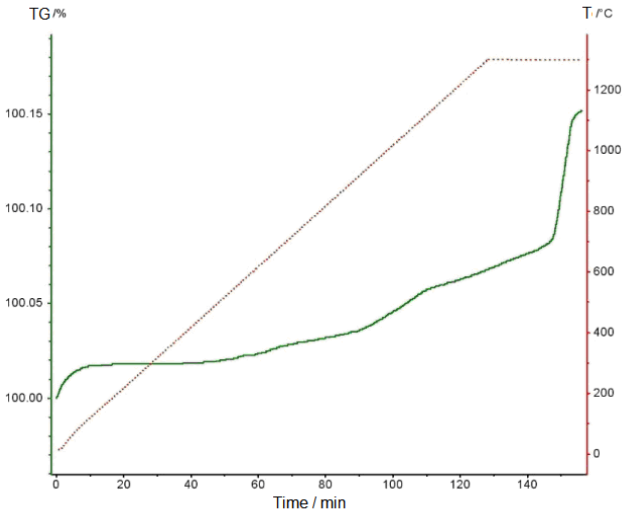

Figure 1. A typical thermogravimetric curve of the uranium dioxide sample oxidation.

Thus, following samples were obtained: O / U = 2.005, O / U = 2.015, O / U = 2.033.

3. Determination of the thermal diffusivity and thermal conductivity of the obtained samples

Measurements of the specific heat and thermal diffusivity were held at Netzsch LFA 427 by laser flash method in a vacuum.

The temperature dependence of heat capacity is shown in figure 2.

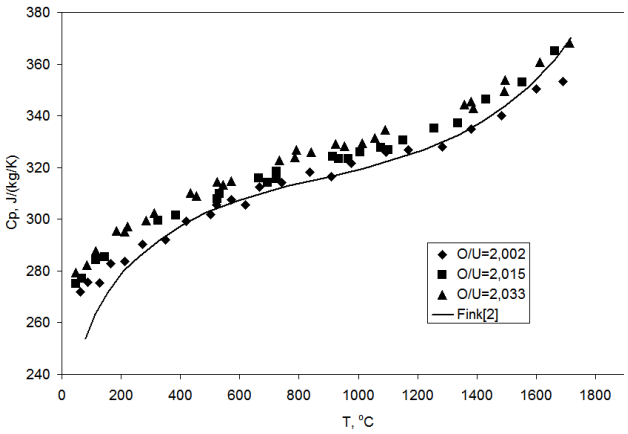

Figure 2. The heat capacity of UO_2 samples.

The heat capacity of the samples increases with temperature from 270 up to 370 J/(g·K) and does not differ more than 5% from each other. The heat capacity of the sample with O / M = 2.002 in good agreement with the results presented in the paper [2].

From obtained data of thermal diffusivity, specific heat and density using the expression (1) were calculated temperature dependence of the thermal conductivity.

$$\lambda(t) = a(t) \cdot C_p(t) \cdot \rho(t). \quad (3)$$

The obtained data are recalculated to 95% TD by the expression

$$\rho_p = \rho_{100}(1-p)^{2,5} \text{ [3]}. \quad (4)$$

Thus calculated temperature dependences of the uranium dioxide thermal conductivity are shown in figure 3.

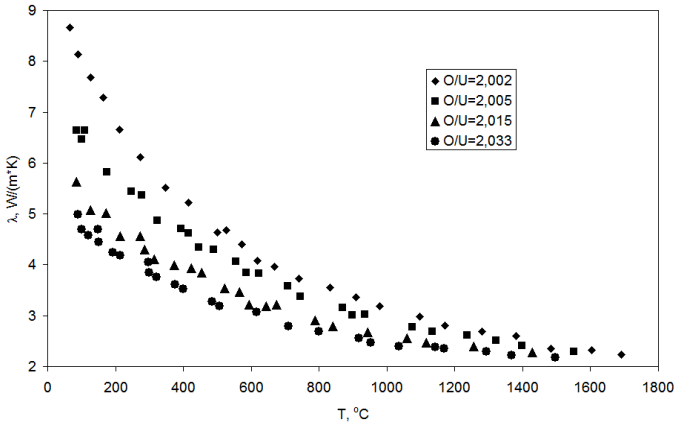

Figure 3. The thermal conductivity UO_2 samples of all compositions.

As is well known the thermal conductivity of ceramic materials above room temperature is determined by the phonon component. In Clemens model [4] it is assumed that the thermal conductivity of the material depends of phonons by phonons and by lattice defects scattering. In hyperstoicheometric uranium dioxide oxygen ions are located in the interstices of the anion sublattice

and stand as phonon scattering centers. In addition to each embedded oxygen atom two uranium ions should change their valence from U +4 to U +5, the atomic radius of the ion U +5 (r = 88.0 pm) smaller than U +4 radius (r = 101.1 pm), thus pentavalent uranium ions are also centers of phonon scattering.

Calculated from the obtained thermal conductivity values, thermal resistance values for all samples are shown in figure 4. It can be seen that the curves are linear, but with increasing of stoichiometry the temperature for which linearity is preserved decreases, such as for O / U = 2.033 linearity is preserved only to 1200 ºC.

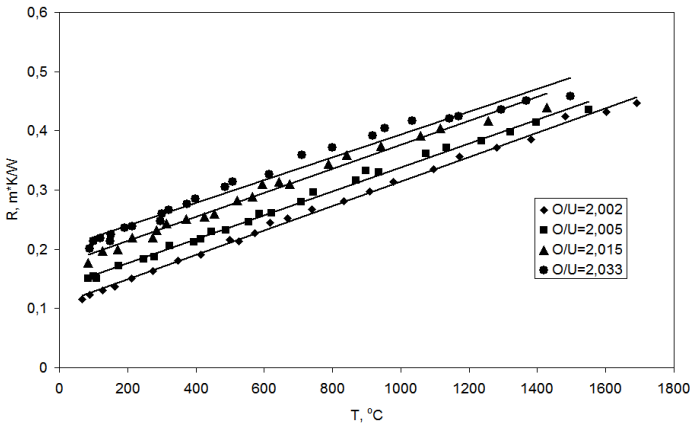

Figure 4. Thermal resistance UO_2 samples of all compositions.

The linearity of the thermal resistance means that the main component of the thermal conductivity is a phonon, and it can be described by the expression (5).

$$R = \frac{1}{\lambda} = A + BT \tag{5}$$

The coefficients *A* and *B*, determined by least squares method are reported in table 2.

Table 2. Coefficients in thermal resistance equation.

	$UO_{2.002}$	$UO_{2.005}$	$UO_{2.0015}$	$UO_{2.0033}$
A, 10^{-2}, m·K/W	4.626±0.014	7.311±0.022	10.697±0.032	13.048±0.039
B, 10^{-4}, m/W	2.121±0.006	2.134±0.006	2.067±0.006	1.998±0.006

The experimental data was processing to obtain the following expression for the thermal conductivity of uranium dioxide, depending of the stoichiometry and temperature (6).

$$\lambda_{95}(T,x) = \frac{1}{A(x) + B(x)T} + \lambda_{electron} = \\ = \frac{1}{(4,627 + 0,55 \cdot x^{1/2}) \cdot 10^{-2} + (2,120 - 3,3 \cdot x) \cdot 10^{-4} \cdot T} + \frac{6400 \cdot 1000^{5/2}}{T^{5/2}} \exp\left(-\frac{16350}{T}\right) \tag{6}$$

4. Conclusions

In this paper, was developed a method of oxidation pure uranium dioxide to a predetermined value O / U by thermogravimetric method on NETZSCH STA 409 with a solid galvanic cell for controlling the oxygen potential of purging gases. For samples obtained after oxidation were determined temperature dependence of the specific heat and thermal diffusivity by laser flash method. Then thermal conductivities were counted for each deviation from stoichiometry.

Thermal conductivity is strongly dependent on the deviation from the stoichiometry because of the formation of interstitial oxygen ions and pentavalent uranium ions that are centers of phonon scattering. From obtained dependences of thermal conductivity were calculated the thermal resistance of uranium dioxide samples of all compositions. Processing of these curves yielded the expression (6) to calculate the thermal conductivity in dependence of temperature and deviations from stoichiometry.

Acknowledgements
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