RESEARCH ARTICLE

Study on Detection Method of Oxygen-Uranium Ratio of UO2-MO Pellets

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Abstract: In this paper, the determination method of the atomic ratio of oxygen to uranium in UO2-MO pellets was studied. Through the experiments of UO2-MO pellets with different composition ratios, the results showed that MO in UO2-MO pellets was a stable compound and did not participate in the thermogravimetric reaction. Only uranium dioxide was oxidized into stable uranium trioxide in oxygen. By accurately measuring the net weight of samples after dehydration and the total weight after oxidation, the formula for calculating the oxygen-uranium ratio of UO2-MO pellets is derived by formula derivation, and the RSD of this method is better than 0.13%.
Keywords: UO2-MO pellets; heat; uranium ratio

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1 Introduction

Although the oxide nuclear fuel used at present can run stably and safely, there is a major drawback that its thermal conductivity is poor, which limits the power of the reactor, causing premature rupture of fuel pellets and fuel deterioration. In order to solve this problem, a mixed process pellet of uranium oxide and MO with better thermal conductivity is developed. In this fuel pellet, MO absorbs heat like a heat pipe, which promotes more effective cooling of the fuel pellet and makes the thermal conductivity of fuel at least 50% higher than that of conventional nuclear fuel [1]. For the pellets with higher thermal conductivity, the detection method is studied correspondingly. In this paper, the oxygen-uranium ratio detection method of UO2-MO pellets is studied.

2 Method Principle

Conventional uranium dioxide is oxidized into stable uranium trioxide in oxygen. The atomic ratio of oxygen to uranium is calculated by accurately measuring the net weight of dehydrated uranium dioxide sample and the weight of oxidized uranium trioxide. According to the quality change and impurity content of uranium dioxide oxidized into uranium trioxide, the atomic ratio of available oxygen to uranium is calculated.

$$\mathrm{UO}_X + O_2 \rightarrow U_3O_8 \tag{1}$$

Uranium atomic ratio [2]:

$$X = 2 + \left(m_{A1}\frac{W_0 - W_0 I_0}{W_t - W_t I_t} - m_{A2}\right) \tag{2}$$

Type-the net weight of uranium dioxide sample before oxidation;W_0——Net weight of uranium dioxide sample before oxidation;

W_t—— The weight of uranium dioxide oxidized into uranium octaoxide.

I_0—— The total weight of oxides of all impurity elements in every gram of uranium dioxide; —— The total weight of oxides of all impurity elements in every gram of U3O8;I_t——Total weight of oxides of all impurity elements per gram of U3O8;

m_{A1}—— The molecular weight of U3O8 /3 times the atomic weight of oxygen;

m_{A2}—— Molecular weight/oxygen atom of uranium dioxide

Among them, the atomic weight of oxygen M0=15.9994, and the atomic weight of uranium is based on the sum of the product of isotope enrichment of each uranium in the sample and its mass fraction:

Mu=234.0409×(234U%)+235.0439× (235U%)+236.0457×(236U%)+238.0508× (238U%) If the sample is natural uranium, 238U accounts for 99.3% and 235U accounts for 235U.

MU =235.0439×0.7%+238.0508×99.3%=238.03

MO in UO2-MO pellets is a stable oxide in oxygen and does not participate in the reaction.

3 Equipment and Materials

The experimental instrument is German relaxation TG209+ASC thermogravimetric analyzer, the temperature range is RT-1000℃ , and the heating rate is (0 ~ 100)℃ / min.

The pellets used in the test are heavy water grinding pellets, which are oxidized with MO powder in a certain proportion.

4 Results and Discussion

4.1 Test Conditions

The selection of test conditions is essential in thermal analysis. The influencing factors of thermal analysis include temperature, atmosphere, gas flow rate, heating rate, etc. Based on the detection method of oxygen-uranium ratio of uranium dioxide powder and pellets, this paper establishes the detection method of oxygen-uranium ratio of UO2-MO pellets.

4.1.1 Temperature Correction

When using thermal analyzer to measure the oxygen-uranium ratio of UO2-MO, it is necessary to ensure the accurate temperature control of the instrument, so it is necessary to carry out temperature correction.

Select In, Sn, Bi, Zn and Al materials provided by Nachi Company, know the theoretical melting point values of these materials, and set the corresponding temperature-raising program (in air atmosphere, it is only necessary to raise the temperature from room temperature to a temperature 50 ℃ higher than the melting point of materials), so that the materials can reach the melting point during the temperature-raising process. The experimental value of melting point of materials can be judged by heat absorption and release, compared with the theoretical value, and corrected to obtain the temperature correction curve. The data results are shown in Table 1.

Table 1 Temperature correction

	Temperature correction		
material	Theoretical value (℃)	Experimental value (℃)	Calibration value (℃)
In	156.6	154.8	156.6
Sn	231.9	228.0	230.9
Bi	271.4	268.5	272.0
Zn	419.5	413.8	419.2
Al	660.3	652.8	660.6

It can be seen from Table 1 that the corrected temperature is very close to the theoretical temperature, and the difference between them is ≤ 1 ℃ , which shows that the temperature control of the instrument is accurate.

4.1.2 Measuring Atmosphere

All the experiments were carried out in dynamic atmosphere. In the dehydration stage of samples, high purity nitrogen was introduced into the furnace for protection. In the oxidation stage, high purity oxygen is introduced to facilitate the complete oxidation of the sample. In the process of measurement, ensure the stability of air flow, otherwise it will affect the TG curve.

4.1.3 Temperature Procedure

In oxygen atmosphere, the sample can be completely oxidized into stable U3O8 from room temperature to 500 ℃ . After the complete oxidation, the weight of the sample does not change, showing a horizontal straight line on the TG curve.

The temperature measurement procedure is as follows: $30℃ \xrightarrow{\text{nitrogen}} 150℃ \xrightarrow{\text{oxygen}} 500℃$, the heating rate in the whole process is 10℃ /min.

4.1.4 Baseline

The apparent weight of sample holders and crucibles that do not undergo any chemical changes under the action of heat will change with the change of temperature, which is the so-called “buoyancy effect”, which is the result of convection caused by the decrease of air buoyancy caused by heating and the thermal effect of mechanical parts of the balance. In order to eliminate the buoyancy effect, it is necessary to measure the baseline of the empty crucible, and then use the baseline to correct the measurement curve of the sample. It should be noted that the measurement of baseline file must have exactly the same measurement conditions, temperature procedures and measurement steps as the measurement of samples.

4.2 Oxygen-uranium Ratio Test

Weigh with a balance of 0.01mg accuracy, test with uranium dioxide pellet grinding powder and MO powder (MO content is 3%, 5%, 7%, 10%), put them into a crucible, and measure the TG curve in a thermogravimetric analyzer. The test results are shown in Table 2.

It can be clearly observed that the higher the MO addition ratio, the lower the weight gain percentage. Fig. 1 shows the thermogravimetric curve of UO2 pellets.

Fig. 1 shows that with the increase of temperature, ura-

Table 2 The weight increase of UO2-Mo pellets after thermal analysis and the ratio of oxygen to uranium

MO		1 measurement	Measurement 2	Measurement 3	Measurement 4	Measure 5	Measurement 6
0	Total weight gain%	3.95	3.96	3.94	3.94	3.95	3.93
	Uranium ratio	2.000	1.999	2.000	2.002	2.000	2.004
3%	Total weight gain%	3.81	3.83	3.82	3.84	3.82	3.81
	UO2 weight gain%	3.92	3.95	3.94	3.96	3.94	3.92
	Uranium ratio	2.005	2.000	2.002	1.999	2.002	2.005
5%	Total weight gain%	3.75	3.73	3.76	3.74	3.76	3.75
	UO2 weight gain%	3.95	3.93	3.96	3.94	3.96	3.95
	Uranium ratio	2.000	2.004	1.999	2.002	1.999	2.000
7%	Total weight gain%	3.65	3.67	3.66	3.67	3.66	3.67
	UO2 weight gain%	3.93	3.95	3.94	3.95	3.94	3.95
	Uranium ratio	2.004	2.000	2.002	2.000	2.002	2.000
10%	Total weight gain%	3.55	3.54	3.55	3.54	3.56	3.56
	UO2 weight gain%	3.94	3.93	3.94	3.93	3.96	3.96
	Uranium ratio	2.002	2.004	2.002	2.004	1.999	1.999

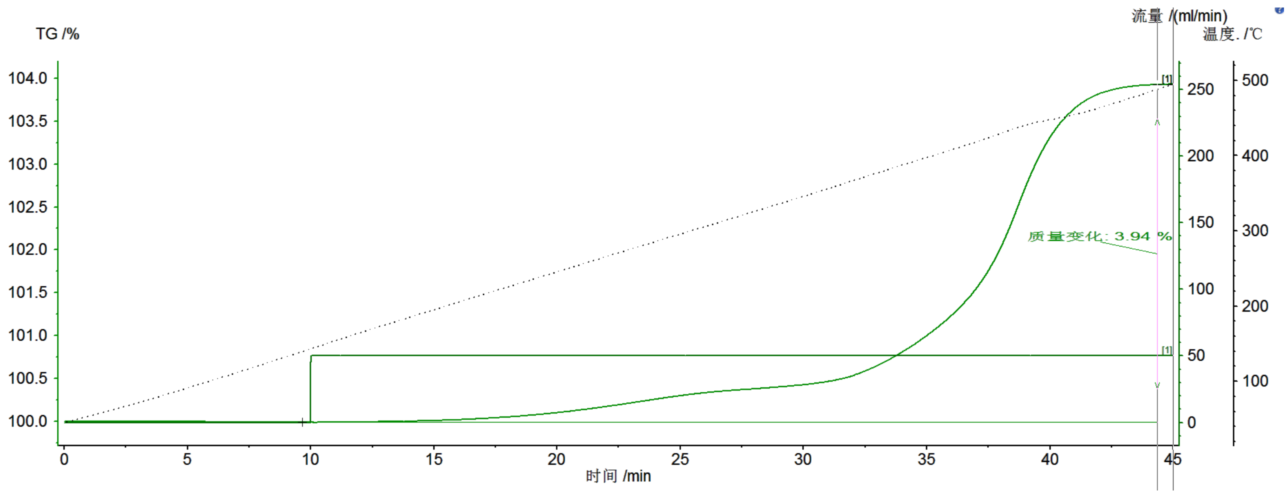

Fig. 1 Thermogravimetric curve of UO2 pellets

nium dioxide is an unstable uranium oxide, and with the increase of temperature, uranium dioxide will be transformed into more stable uranium trioxide, which shows an increase in mass. According to the national standard GB 11842 “Determination of oxygen-uranium atomic ratio of uranium dioxide powder and pellets by thermogravimetric method”, the weight gain percentage can be measured. The thermogravimetric curve of MO-doped uranium dioxide pellets is the same as that in fig. 1, but the difference is that the weight gain will change with the addition of MO.

The atomic ratio of oxygen to uranium is calculated by formula (1) and (2). After the grinding powder of uranium dioxide pellets is doped with MO, only uranium dioxide generates uranium trioxide. With the increase of MO content, the corresponding content of uranium dioxide decreases, and the weight gain decreases. According to the above analysis, for the calculation of oxygen-uranium ratio of uranium dioxide -MO pellets, the formula is used to deduce: the calculation formula of total weight gain percentage.

$$\Delta w = \frac{W_t - W_0}{W_0} \tag{3}$$

Type-total weight gain percentage Δw—Total weight gain percentage

W_0—is the total weight of the sample before oxidation.

W_t—is the total weight of the sample after oxidation.

2 UO weight gain percentage calculation formula:

$$\Delta w_{UO_2} = \frac{\Delta w}{w_{UO_2}} = \frac{\Delta w}{1-w_{BeO}} \tag{4}$$

Type-weight percentage of uranium dioxide w_{UO_2}—Percentage of uranium dioxide by weight

w_{MO}—weight percentage of mo

According to the formula, the uranium dioxide -MO oxygen-uranium ratio with different addition ratios can be calculated.

The net weight percentage of UO2-MO pellets is almost the same as that of UO2-MO pellets, and the calculated oxygen-uranium ratio is the same, which fully proves that MO in UO2-Mo pellets does not participate in the weight gain reaction.

The oxygen-uranium ratio of UO2-5%MO pellets provided in the process is measured. The mass spectrometer is used to measure the actual content of MO in UO2-5%MO pellets provided in the process to be 4.95%, which is close to the theoretical value. After calculation, the oxygen-uranium ratio of UO2-5%MO pellets is 2.000, which is consistent with the oxygen-uranium ratio of uranium dioxide pellets without MO.

4.3 Precision

Using the above measurement conditions, 5% UO2-MO was measured for 6 times, and the measurement results are shown in Table 3.

Table 3 Precision test

Test times	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	average value	RSD%
Uranium ratio	1.997	1.999	2.000	2.002	2.004	2.000	2.000	0.13

The RSD of the method is better than 0.13%.

5 Conclusion

1 The results show that the oxygen-uranium ratio of uranium dioxide doped with MO is basically the same as that without MO, and MO in UO2-MO pellets is a stable compound and does not participate in thermogravimetric reaction. Through formula derivation, the calculation formula of oxygen-uranium ratio of UO2-MO pellets is obtained.

2 The RSD of the established method is better than 0.13%, and the reliability of the method is verified by UO2-5%MO pellets.

References

[1] Wu Haosong, News of American engineers developing safer and more efficient nuclear fuel, 2005, (10): 25-26