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Methodological Features of Uranium Mononitride Evaporation by Thermogravimetry

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Abstract

Choice of evaporation regimes and sample area influence are the most important factors during high-temperature tests of uranium mononitride. It is shown that as the sample area increases, the rate of mass loss is also rises. Significant increase in the rate of mass loss is observed with test regime change: study sample on the substrate at the top of the crucible instead at the bottom of the crucible. These experiments are in agreement with the theoretical concepts of uranium nitride evaporation kinetics. Thus, it is necessary to make amendment for the surface area of the samples, as well as take into account evaporation regimes of the experiments to compare different results of thermal stability.

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1. INTRODUCTION

Earlier, we conducted studies of uranium mononitride behavior at high temperatures in helium [1]. A technique based on thermogravimetry has been developed, which makes it possible to study the evaporation and decomposition of uranium-containing nitride fuel. Despite a number of successfully received data, the methodology required further development. This is due to the fact that the microstructure of the UN samples obtained after the experiments had significant differences for different experiments, which brought some misunderstanding. Thus, in the method it is necessary to show the influence of the surface area of the samples of UN on the kinetics of evaporation. Also it is necessary to show the influence of the surface area of the UN samples on the kinetics of evaporation in our technique. The vaporization of uranium mononitride is also investigated by Knudsen effusion cell mass spectrometry [2-4]. This technique is

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fundamentally different from our work [1], since the main aim was to reveal thermodynamic parameters of evaporation but it is impossible to obtain data about kinetics. This paper is a continuation of the study of UN evaporation kinetics.

2. EXPERIMENTAL REVIEW

Thermal stability experiments at high temperatures were carried out in a synchronous thermal analyzer Netzsch STA 449 F1 in a stream of high-purity helium (mark 6.0, pressure 1 bar) at a rate of 100 ml/min. The heated purifying getter MonoTorr was used to further reduce the amount of impurities in helium <1 ppb. Experiments in STA were carried out with thermogravimetry mode, which makes it possible to determine as accurately as possible the loss of mass of the sample during heating, depending on time and temperature. In this mode we use a tungsten crucible with a diameter of 7 mm, so that samples of various configurations can be freely placed in it. The crucible weight was about 1.25 g. The temperature of the sample and the furnace was determined by two thermocouples of W-Re alloys.

The temperature program for sample heating was selected based on the expected decomposition characteristics of the pure UN and from the experience of previous studies. After the test experiments, it was decided to use the temperature program with the lowest holding time, at which a constant evaporation rate is reached: 15 minutes at 2100 °C. Algorithm for studying of the UN samples is next: 1. Annealing of the holder and the crucible in a vacuum at a temperature of 2200 °C for 30 minutes; 2. Correction according to the experimental program with an empty crucible; 3. Testing of the UN sample according to the correction program. This algorithm was repeated for each sample.

Dependence on the surface area. Several samples were prepared with different area: scatter no more than 20%. However, after the experiments, the correlation between the change in the rate of mass loss and with the area of samples was not observed due to the scatter of the obtained data. Then, two consecutive experiments were carried out: one sample was twice as large as the other (50 and 100 sq.mm). The figure below shows that the rate of mass loss of a larger sample also doubled.

In the series of experiments just described, the sample was studied at the bottom of the crucible, as shown in Figure 2a. In the further part of the work, the sample was tested on the top of the crucible, using a tungsten substrate (Figure 2b). This design eliminates the effect of the crucible walls on the process of removing evaporated nitrogen from the sample.

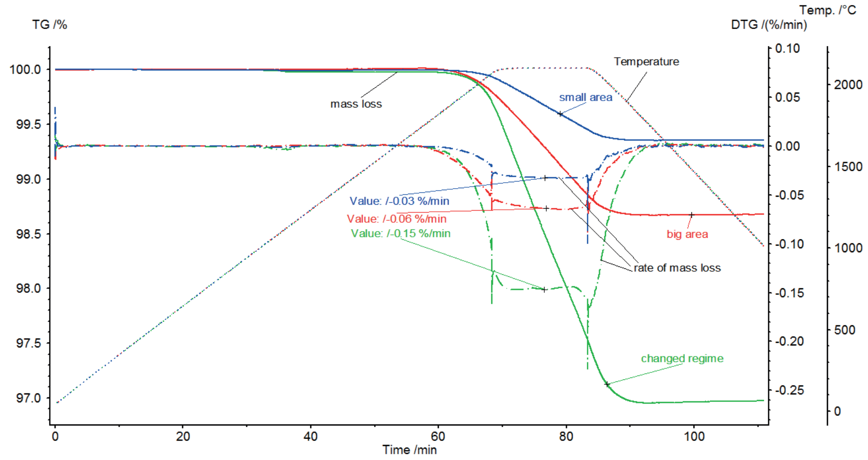

Figure 1: Thermogravimetric data of UN samples with different surface area and modified evaporation regime.

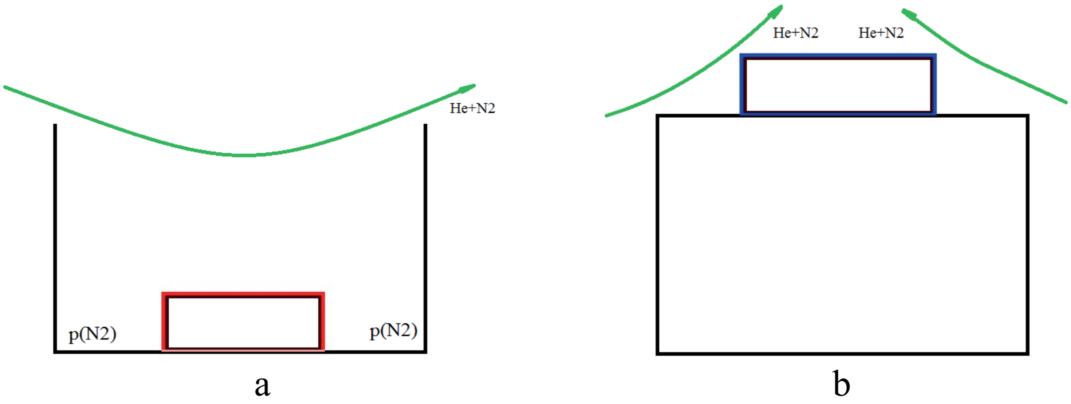

Figure 2: Changed regime of UN investigation: sample at the bottom of the crucible (a), sample on the substrate at the top of the crucible (b).

The obtained thermogravimetric results are shown in the Figure 1. It can be seen that the beginning of the mass loss in this case is also about 1800 °C, however, evaporation rate has significantly increased: 2.5 times and 5 times as compared to the measurement at the bottom of the crucible.

The amount of liquid uranium is much less for the sample studied at the bottom of the crucible (Figure 3a). In addition, at this regime a new phase was released in the form of spherical precipitates in the body of grains. In the case of a study on the substrate at the top of crucible new phase predominates anly at the grain boundaries. Consequently, taking into account the more aggressive impact of the medium, the microstructure in Figure 3b represents a later stage of the decomposition process of the uranium mononite, in which occurs either the movement of uranium precipitates from the grain body, or the liquid is immediately released at the grain boundaries.

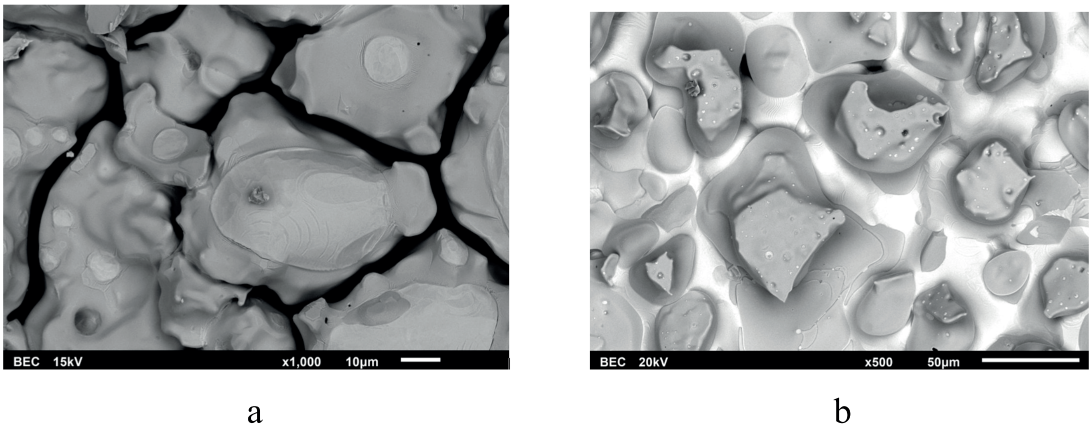

Figure 3: Scanning electron microscopy of the sample investigated at the bottom of the crucible (a) and on the substrate at the top (b).

3. DISCUSSION

Based on the experimental results, it was shown the explicit dependence of the surface area and the rate of UN mass loss. This fact agrees with the theoretical premises. As stated above, the experiments were carried out in a helium medium with a definite partial pressure of nitrogen, which significantly influenced on evaporation. The total pressure of the atmosphere is also important, since it determines the mean free path of the evaporated particles. If the total pressure is small and the mean free path is made commensurate with the dimensions of the crusible in which evaporation occurs, the amount of vaporized material can be calculated. In the case of a number of assumptions on the experiments in this paper, we can estimate the evaporation rate from the Langmuir-Knudsen formula.

$$W = -\frac{1}{s}\frac{dm}{dt} = kp_1\sqrt{\frac{M}{2\pi RT}} \tag{1}$$

where W is the evaporation rate; m is the mass of the evaporated material; τ - duration of evaporation; s is the evaporation surface; p_1 - equilibrium partial pressure of the main evaporating component (depends on the content of impurities in the sample); M is the molecular weight; T is the temperature of the evaporation surface; $0 < k < 1$ is the correction factor (which includes a significant number of parameters that can affect the evaporation process in a real experiment: the microstructure of the samples, the reaction products removing rate, etc.).

In this paper, the formula can be applied if we take into account in the correction coefficient the presence of an atmosphere-helium, with a pressure of 1 bar, which naturally builds up to above the sample. Rewriting formula 1, we get:

$$\frac{dm}{d\tau} = skp_1\sqrt{\frac{M}{2\pi RT}} \tag{2}$$

In a series of experiments, only one parameter was changed: s. Remaining parameters p_1 and k, may vary slightly depend due to the difference in the structure of the samples or, for example, in case of insufficient pumping of the STA furnace (presence of foreign gases in the carrier gas). Proceeding from this formula, it is clear that the rate of mass loss will linearly depend on the surface area of the sample. As shown in Figure 4, if we take into account statistical error, we can see that statement.

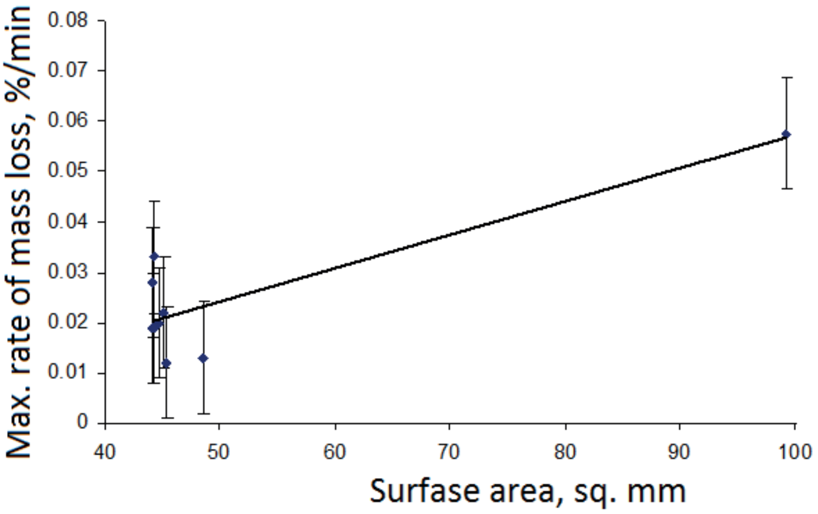

Figure 4: Experimental dependence of mass loss rate on surface area.

Behavior of evaporation process after changing investigation regime can be explained as follows. Released nitrogen from the UN in ideal case is almost immediately removed at a sufficiently remote distance from the sample surface. That' why partial nitrogen pressure above the sample will be equal to the partial nitrogen pressure in the purge gas (helium): $p_{N2\text{(above sample)}} = p_{N2\text{(in He)}}$.

However, in real conditions, this equality can not be fulfilled. Atoms and molecules of nitrogen will suffer collide with He atoms and return back to the sample. This effect will lead to increasing of nitrogen partial pressure above the sample: $p_{N2\text{(above sample)}} > p_{N2\text{(in He)}}$.

In the case shown in Figure 2a, in addition to the above process, the crucible walls will also affect the increase in the nitrogen partial pressure above the sample. The released nitrogen will reflect from the walls of the crucible, will back to the sample and will raise the partial pressure above the sample. Thus, significant increase of evaporation rate in the last experiment is associated with a more efficient removal of nitrogen from the surface of the sample.

4. CONCLUSIONS

Evaporation of uranium mononitride was investigated using a synchronous thermal analyzer Netzsch STA449 F1. Experiments showed when the surface area of the UN is doubling, mass loss rate also increase from 0.03 %/min to 0.06 %/min. However, due to the scatter of the experimental data, it is not possible to determine the correlation of mass loss rate and the area (in the case of its variation up to 20%). According to the Langmuir-Knudsen equation, in the absence of a change in the composition of the material and the partial pressure in the atmosphere, the dependence of the evaporation rate increases linearly with increasing area. The latter is satisfied, taking into account the error in this series of experiments. The change in the evaporation regime of uranium mononitride samples allowed a higher level of thermogravimetry signal, as well as a structure corresponding to the settled evaporation process.

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