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Modeling of Phase Separation in Uranium Mononitride

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Abstract

Semiempirical modeling of uranium mononitride decomposition was carried out using the laws of the chemical kinetics of heterogeneous reactions. All calculations based on results received from thermal stability tests of UN at high temperatures. Kinetic curves of UN decomposition products correspond to the self-accelerating decomposition, which follows the induction period. The experimental data of uranium nitride mass loss in the investigated range of parameters are well described obtained results. The modeling can be used to estimate the phase composition of uranium mononitride during high-temperature tests in an atmosphere that does not contain nitrogen.

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1. INTRODUCTION

Modelling of uranium mononitride behavior at high temperatures is necessity to prediction of fast neutron reactors operation, as well as nitride fuel fabrication. Numerous experimental data give direct output data about UN behavior but this is not enough to calculate UN behavior even with insignificant deviations in external conditions. Thermodynamic modeling of the U-N system was carried out in paper [1]. The initial data were the fundamental thermodynamic properties of all possible connections of this system, available in databases. Consistent sets of Gibbs energies for different phases at atmospheric pressure were obtained by specialized software package. The resulting relations were consistent with the experimentally obtained phase diagram. In another paper [2], behavior of actinide nitrides fabrication was calculated on the basis of the ALCHYMY database. Authors showed that practical difficulties can be avoided only when equilibrium parameters are reached, i.e. thermodynamically However, when considering the kinetics, the modeling will change dramatically. In this paper, modeling based on chemical kinetics was conducted, using the experimental data of uranium mononitride decomposition obtained earlier [3, 4].

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2. EXPERIMENTAL

Decomposition of uranium mononitride in high-purity helium at high temperature involves two distinct stages. Direct decomposition:

$$2UN(s) \rightleftarrows 2U(l) + N_2 \tag{1}$$

In this process, gaseous nitrogen is released from the surface of uranium mononitride into the helium atmosphere. A high flow rate of helium will capture and carry away this nitrogen. To simplify the construction of the model, we will assume that nitrogen instantaneously will be removed from the sample. the nitrogen released from the sample will instantaneously carry away the flow of helium. As a result, the system can set a constant value of the partial pressure of nitrogen (in helium): p$_{N2(He)}$, which will be significantly lower than the equilibrium partial pressure of nitrogen over UN(s) - p$_{N2(UN).}$ Thus, there will be no thermodynamic equilibrium until all the material decomposes in the system. This assumption also makes it possible to transform equation (1) into the form of an irreversible reaction:

$$2UN(s) \rightarrow 2U(l) + N_2(g) \tag{2}$$

It should be noted that the main driving force of decomposition will be the difference of these partial pressures:

$$F_{pa3\pi o\mathscr{H}eHuR} \sim \left(p_{N_2(UN)} - P_{N_2(He)}\right) \tag{3}$$

Next, the evolved liquid phase of uranium will evaporate:

$$U(l) \rightarrow U(g) \tag{4}$$

At temperature corresponding to decomposition of uranium mononitride (> 1750 °C in He), the separated phase of uranium is in a liquid state (T$_m$(uranium) = 1132 °C). However, the boiling point of uranium is 4131 °C. Nevertheless, at temperature much higher than the melting point, uranium evaporates at a rather high rate, since the pressure of saturated uranium vapor increases significantly with increasing temperature: at 1100 °C - 10$^{-12,7}$ atm, and at 2000 °C - 10$^{-2,4}$ atm (for example, at 100 °C - 10^{-65} atm). The partial pressure of saturated UN(g) vapor over uranium mononitride at the same temperature is 10$^{-9.2}$ atm. Consequently, the evaporation of uranium and release of nitrogen gas will be much faster than the sublimation of compound UN(s). Since the mass of nitrogen is much lower than the mass of uranium, on experimental thermogravimetric curves the main contribution to mass loss possible will be the evaporation of uranium (already from the liquid phase).

Previous experiments [3, 4] using Netzsch STA 449F1 (synchronous thermal analysis device) showed that decomposition on the surface of the samples with the precipitation of liquid uranium is occurs as a result of heating uranium mononitride in helium. Typical thermogravimetric curves (Figure 1), are indicate the uniformity of the mass loss process. Based on the obtained data we can't divide the reactions occurring during the decomposition.

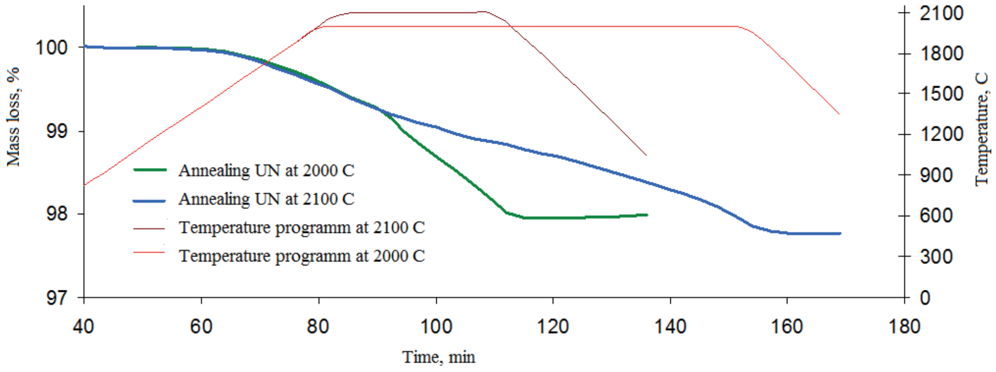

Figure 1: Thermogravimetric data of uranium mononitride sample (during heating and isothermal annealing at 2000 and 2100 °C).

3. MODELLING BASED ON CHEMICAL KINETICS

Decomposition of uranium mononitride is a system of two successive heterogeneous reactions containing a solid, liquid and gaseous phase.

$$\begin{cases} 2UN(s) \rightarrow 2U(l) + N_2(g) \\ U(l) \rightarrow U(g) \end{cases} \tag{5}$$

The reaction rates can be expressed in terms of the first derivative of the concentration of any participating substance in the reaction with respect to time. Due to the fact that the substances react in stoichiometric amounts, reactions (5) can be written:

$$\frac{dC_{UN(s)}}{dt} = -2w_1, \quad \frac{dC_{N2}}{dt} = w_1, \quad \frac{dC_{U(l)}}{dt} = 2w_1 - w_2, \quad \frac{dC_{U(g)}}{dt} = w_2 \tag{6}$$

where $C_{UN(s)}$, C_{N2},$C_{U(l)}$,$C_{U(g)}$ are the concentrations of the initial substances and reaction products, w_1 and w_2 are the rates of reactions in system 5, that is, we recorded a change in the concentration of substances (reagents or products) per unit time.

According to the basic position of chemical kinetics, the reaction rate at each instant of time is proportional to the product of the concentrations of the reacting substances. Then the equations of velocities for system 5 can be written:

$$w_1 = k_1 C_{UN(s)}, \quad w_2 = k_2 C_{U(l)} \tag{7}$$

where k_1 and k_2 are reaction rate constants, which, like the reaction rate, depend on many factors: the nature of the reagents, pressure and temperature, catalysts, diffusion, porosity, composition and structure of the material, as well as a number of other factors associated with the specific reaction conditions (material shape, heating mode, etc.). The physical standing of the initial substances and reaction products can produce a strong effect on the rate of chemical reaction.

It is necessary add the Arrhenius dependence to the reactions of system 5, which will include the formation energy of reactions in the system 5:

$$k_1 = Ae^{-\frac{G_1}{R \cdot T}}, \quad k_2 = Be^{-\frac{G_2}{R \cdot T}} \tag{8}$$

where G_1 and G_2 are the formation energies of the UN(s) and evaporation U(l). Constants A and B - include the entire spectrum of properties and characteristics included in the reaction rate constants and are usually chosen from experimental values. For simplicity, the energy of formation and evaporation were taken as constants.

Thus, substituting 8 in 7, and then obtaining equation in 6, we can write system of differential equations. Initial conditions for the system:

$$C_{UN(s)} = 1, \quad C_{N2} = 0, \quad C_{U(l)} = 0, \quad C_{U(g)} = 0 \tag{9}$$

Temperature program (heating, holding and cooling) in the Maple software package was set by the following temperature function:

$$T = i[3] + v[1] \cdot \left(\frac{t}{2} - \left| \frac{i[1]}{2} - \frac{t}{2} \right| + \frac{i[1]}{2} \right) + v[2] \cdot \left(\frac{i[2]}{2} - \frac{t}{2} - \left| \frac{i[2]}{2} - \frac{t}{2} \right| \right) \tag{10}$$

where v[1] and v[2] are the heating and cooling rates, i[1] and i[2] are the start and end of the soak, i[3] is the initial temperature.

Solution of the differential equations system has a complex analytical form, which can be displayed graphically. In the Figure 2, the calculated concentrations of UN, N_2, Ul and Ug, as a function of time, are constructed for experimental data shown in Figure 1. Coefficient A from the equation, adjusted in such way that the slope angle of the model concentration curve UN was close to the experimental thermogravimetric curve. It plays a role only in the process of decomposition. Coefficient B should be selected based on amount of uranium phase precipitation in the UN surface after the experiment. This coefficient contains characteristics of the uranium evaporation. Calculated values of the UN mass loss are in good agreement with the experimental kinetics. When we set in equations final amount of liquid uranium (determined after the test), the model can show how the concentration of UN components changes during decomposition and subsequent evaporation. It is worth noting that the liquid uranium concentration curve in the system passes through a maximum: at the initial stage, its concentration increases, then the decline, due to evaporation. The model takes into account the behavior of the material on a shallow layer. This is due to the fact that the decomposition process occurs only at the phase boundary or on the UN surface in this case.

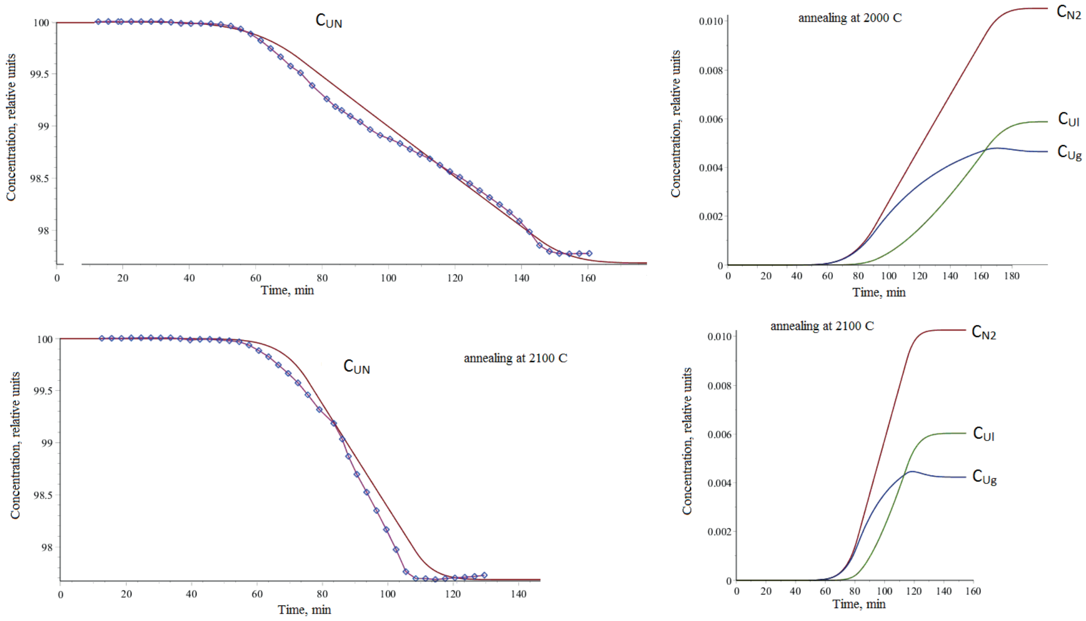

Figure 2: Calculated concentrations of UN decomposition products and comparison with thermogravimetric data.

In view of a number of assumptions, including the lack of diffusion calculation of the nitrogen flux from the material depth, the model gives us only a rough estimate. Obtained results of concentration dependence is in good agreement with the experimental values and sufficiently reliably reflect occurring processes. Obtained curve for UN corresponds to the form of the kinetic curve of the expansion: self-acceleration decomposition, which follows the induction period (according to Figure 3b).

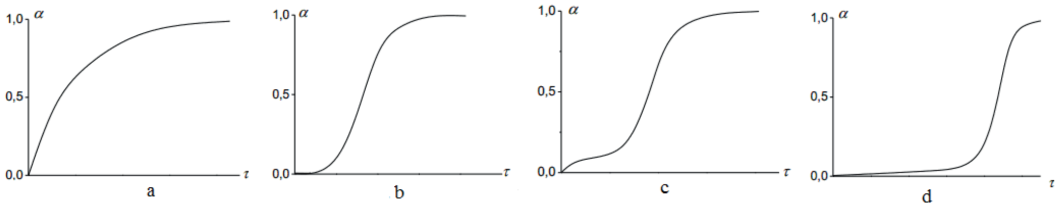

Figure 3: Typical forms of thermal decomposition kinetic curves: a-decomposition without self-acceleration, b-decomposition with self-acceleration, c-induction period corresponds to the decomposition of a small amount of matter, d - is a very slow initial decomposition, which then spontaneously accelerates and proceeds as b,c [5].

4. CONCLUSIONS

Construction of models that can be show kinetic parameters of uranium mononitride decomposition process at high temperatures is a complex and multifactorial task. Semiempirical model obtained in this work relies on the chemical kinetics of heterogeneous reactions, makes it possible to obtain an estimated value of uranium mononitride phase composition during heating, soaking and cooling. It is shown that during the heating of uranium mononitride, both withdrawing nitrogen and evaporating liquid uranium contribute to the mass loss. Beginning of mass loss connected with both components and it is problematic to divide the contribution one of the two components in thermogravimetric data. Further refinement of this model may allow us to show how much nitrogen or gaseous uranium can be released during fabrication or while reactor operating if decomposition conditions of UN are reached.

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