Thermodynamic Analysis of the Carbothermal Synthesis of (U, Pu)N

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Abstract—Thermodynamic modeling was performed to study and evaluate the behavior of the physicochemical system characteristic of the carbothermal synthesis of uranium and plutonium mononitrides. The chemically equilibrium system compositions were calculated for different temperatures, pressures, and nitrogen amounts in the system using HSC Chemistry 7.1 and TeDy programs. The change in the Gibbs energy was calculated for a series of possible reactions, and the equilibrium constants of the chemical reactions were calculated from this quantity. The reactions were evaluated thermodynamically using the equilibrium constants and their temperature dependences.

Keywords: thermodynamic modeling, chemical equilibrium, TeDy, carbothermal synthesis, HSC Chemistry 7.1, nitride nuclear fuel

Mixed uranium–plutonium nitride fuel was chosen in Russia as promising for fast reactors [1]. Interest in this kind of fuel is due to its properties. The nitride fuel exhibits good thermal conductivity, high radiation resistance, and relatively high density, which allows the linear and specific power obtained from fuel elements to be increased.

A process for producing uranium and plutonium mononitrides from oxides by carbothermal synthesis is being developed within the framework of Proryv (Breakthrough) project [1, 2]. The process consists in high-temperature treatment of a mixture of uranium and plutonium oxides with graphite in a nitrogen flow. Detailed mechanism of the carbothermal synthesis reaction is insufficiently understood. Therefore, it is appropriate to perform thermodynamic modeling to study and evaluate the behavior of the physicochemical system characteristic of the carbothermal synthesis, based on the data on the chemically equilibrium compositions. Analysis of the thermodynamic modeling results allows formulation of the directions for experimental and theoretical studies concerning the process mechanism and kinetics.

CALCULATION OF THERMODYNAMICALLY EQUILIBRIUM COMPOSITIONS OF THE SYSTEM

The thermodynamically equilibrium chemical compositions of the system were calculated using the HSC Chemistry 7.1 software [3]. The temperature dependence of the thermodynamically equilibrium composition of the system was calculated in the following setting:

– list of substances included in the system and in the program database: $CCN_{(g)}$, $CH_{4(g)}$, $CN_{(g)}$, $C_2N_{2(g)}$, $CNN_{(g)}$, $CO_{(g)}$, $H_{2(g)}$, $HCN_{(g)}$, $N_{2(g)}$, $NCN_{(g)}$, $NH_{3(g)}$, $Pu_{(g)}$, $PuO_{(g)}$, $PuO_{2(g)}$, $U_{(g)}$, $UO_{(g)}$, $UO_{2(g)}$, $UO_{3(g)}$, PuO_2, UO, U_3O_8, UO_2, PuN, UN, $UN_{1.5}$, $UN_{1.51}$, $UN_{1.55}$, $UN_{1.59}$, $UN_{1.69}$, $UN_{1.73}$, UN_2, U_2N_3, PuC, PuC_2, Pu_2C_3, UC, U_2C_3, C, Pu, PuH_2, PuH_3, U, and UH_3;

– ratio of starting substances: C 2 mol, UO_2 0.8 mol, PuO_2 0.2 mol, and N_2 + 8% $H_{2(g)}$ 2 mol;

– temperature interval from 1300 to 2000°C;

– pressure 1 atm.

The calculation result in the form of the tempera-

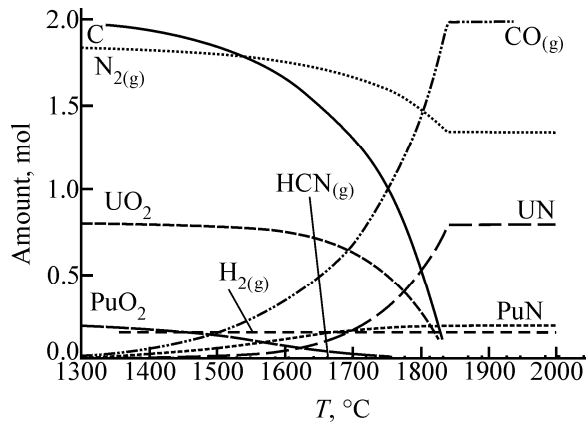[†] Deceased.

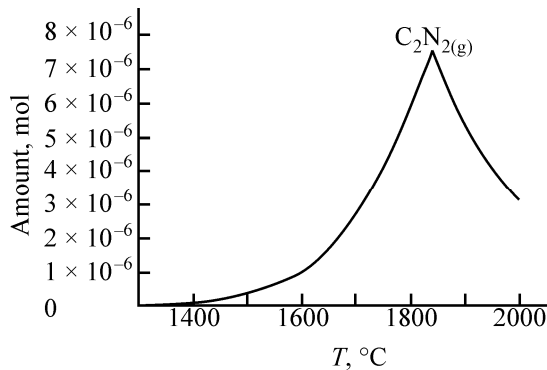**Fig. 1.** Equilibrium composition of the system in the temperature range 1300–2000°C.

Fig. 2. Temperature dependence of the HCN$_{(g)}$ amount.

Fig. 3. Temperature dependence of the (CN)$_{2(g)}$ amount.
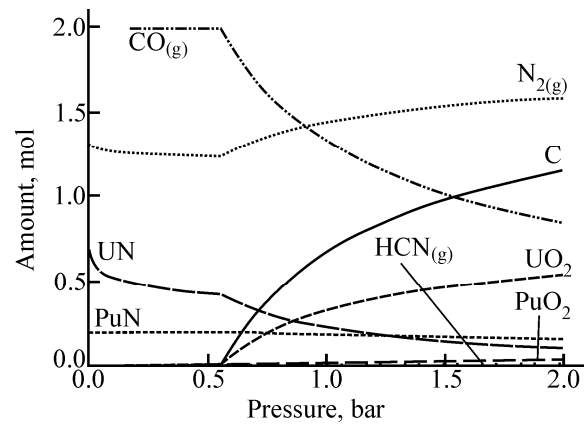
Fig. 4. Equilibrium composition of the system in the pressure range 0.01÷2 atm.

ture dependence of the equilibrium substance amount is shown in Fig. 1.

As can be seen, at temperatures higher than 1300°C the equilibrium starts to shift toward the formation of carbothermal synthesis products, and at 1850°C only the products of the mononitride synthesis reactions remain in the equilibrium mixture.

The presence of hydrogen cyanide is possible in the presence of hydrogen (Fig. 2); HCN can accelerate the synthesis owing to the appearance of an additional mechanism of the carbon transport to the reaction surface. Also, tendency to metallization of Pu and U is observed at temperatures higher than 1400 and 1600°C, respectively.

The cyanogen formation is possible at temperatures higher than 1400°C (Fig. 3). Cyanogen can ensure an additional mechanism of the carbon transport, as in the case of formation of hydrogen cyanide.

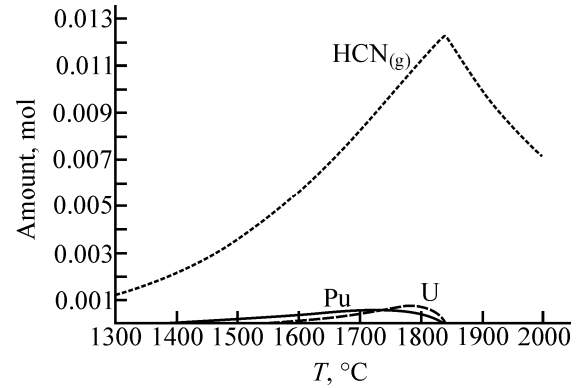A decrease in the pressure in the system also shifts the equilibrium toward formation of uranium and plutonium mononitrides (Fig. 4). The pressure dependence of the equilibrium composition of the system was constructed for the pressure range 0.01–2 atm and isothermal heating temperature of 1750°C. The substance composition of the system is the same as in the first problem.

The influence of the nitrogen amount on the equilibrium composition of the system is shown in Fig. 5. The dependence was plotted for the isothermal heating temperature of 1750°C.

THERMODYNAMIC EVALUATION OF POSSIBLE CHEMICAL REACTIONS

A series of chemical reactions can occur in the course of carbothermal synthesis of nitride fuel from uranium and plutonium oxides [2, 4–9]. To reveal the most probable mechanism of the synthesis, we performed thermodynamic evaluation of the following

set of possible reactions:

$$2C + N_2 \rightarrow (CN)_2,$$
$$C + 1/2\,N_2 \rightarrow CN,$$
$$C + N_2 \rightarrow NCN,$$
$$2C + 1/2\,N_2 \rightarrow CNN,$$
$$C + 2H_2 \rightarrow CH_4,$$
$$N_2 + 3H_2 \rightarrow 2NH_3,$$
$$N_2 + H_2 + 2C \rightarrow 2HCN, \qquad (I)$$
$$2HCN \rightarrow (CN)_2 + H_2,$$
$$UO_2 + 2C + 1/2\,N_2 \rightarrow UN + 2CO, \qquad (II)$$
$$2UO_2 + 5C + N_2 + 2H_2 \rightarrow 2UN + 4CO + CH_4,$$
$$UO_2 + (CN)_2 \rightarrow UN + 2CO + 1/2\,N_2, \qquad (III)$$
$$UO_2 + 3C \rightarrow UC + 2CO,$$
$$UO_2 + 4C \rightarrow UC_2 + 2CO,$$
$$2UO_2 + 7C \rightarrow U_2C_3 + 4CO,$$
$$U_3O_8 + 14C \rightarrow 3UC_2 + 8CO,$$
$$2U + N_2 \rightarrow 2UN,$$
$$U + 2C \rightarrow UC_2,$$
$$U + C \rightarrow UC,$$
$$2U + 3H_2 \rightarrow 2UH_3,$$
$$UC + UC_2 \rightarrow U_2C_3,$$
$$UN + 2C \rightarrow UC_2 + 1/2\,N_2,$$
$$PuO_2 + 2C + 1/2\,N_2 \rightarrow PuN + 2CO,$$
$$PuO_2 + 2HCN \rightarrow PuN + 2CO + H_2 + 1/2\,N_2,$$
$$2PuO_2 + 5C + N_2 + 2H_2 \rightarrow 2PuN + 4CO + CH_4,$$
$$PuO_2 + 3H_2 \rightarrow PuH_2 + 2H_2O,$$
$$2PuO_2 + 7C \rightarrow Pu_2C_3 + 4CO,$$
$$PuO_2 + 3C \rightarrow PuC + 2CO,$$
$$PuO_2 + 4C \rightarrow PuC_2 + 2CO,$$
$$Pu + H_2 \rightarrow PuH_2,$$
$$2Pu + N_2 \rightarrow 2PuN,$$
$$2Pu + 3H_2 \rightarrow 2PuH_3,$$
$$PuC + PuC_2 \rightarrow Pu_2C_3,$$
$$PuH_2 + 1/2\,H_2 \rightarrow PuH_3,$$
$$UO_2 + 2HCN \rightarrow UN + 2CO + H_2 + 1/2\,N_2. \qquad (IV)$$

This list includes substances containing only the elements present in the system under consideration, taking into account the available data on the thermodynamic properties in the temperature range studied. When compiling the list, we also took into account the data from [2, 4–9].

The thermodynamic calculation of the reactions was performed using the TeDy program complex [10–14] on the basis of reference data [15] on the Gibbs
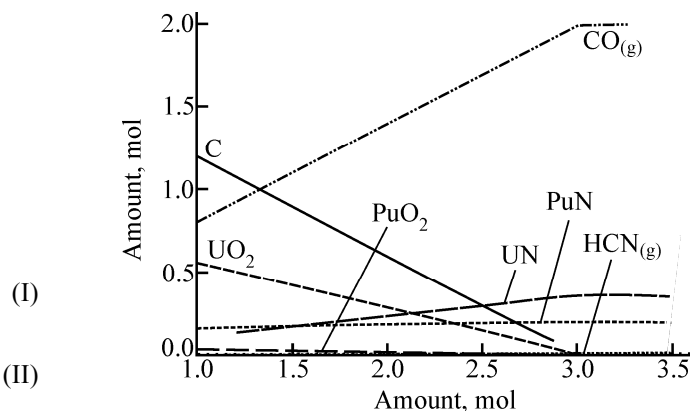

Fig. 5. Equilibrium composition of the system as a function of the $N_{2(g)}$ amount.

energies of the reactants and products of chemical transformations. The change in the Gibbs energy in the course of chemical reactions was calculated using the Hess law. From the changes in the Gibbs energy, we calculated the equilibrium constants of the chemical reactions using the van't Hoff isotherm equation.

The results of calculating the equilibrium constants of chemical reactions that can occur in the course of the carbothermal synthesis are presented as temperature dependences in Fig. 6.

From the equilibrium constants obtained and their temperature dependences, it is possible to determine for each reaction the equilibrium ratio of the reactants and products and the effect exerted on it by external factors such as the process temperature, total pressure in the system, and gas mixture composition.

The results of calculating the thermodynamics of overall reaction (II) between UO_2, C, and N_2 show that such process is thermodynamically unfavorable up to 2200 K, and at 3000 K the equilibrium constant is 2.5×10^3. Hence, to ensure complete synthesis UN, the products should be removed from the reaction zone as completely as possible. Because CO is one of reaction products, its efficient removal from the reaction zone allows the positive driving force of the direct reaction to be maintained permanently. Also, to enhance the driving force of the direct reaction, it is possible to increase the process temperature and, correspondingly, the reaction rate constant. However, the reaction acceleration in this case is restricted by the diffusion factor. With increasing temperature, the rate of the transport of the reactants and products to the reaction zone and from it will increase less steeply than the rate con-
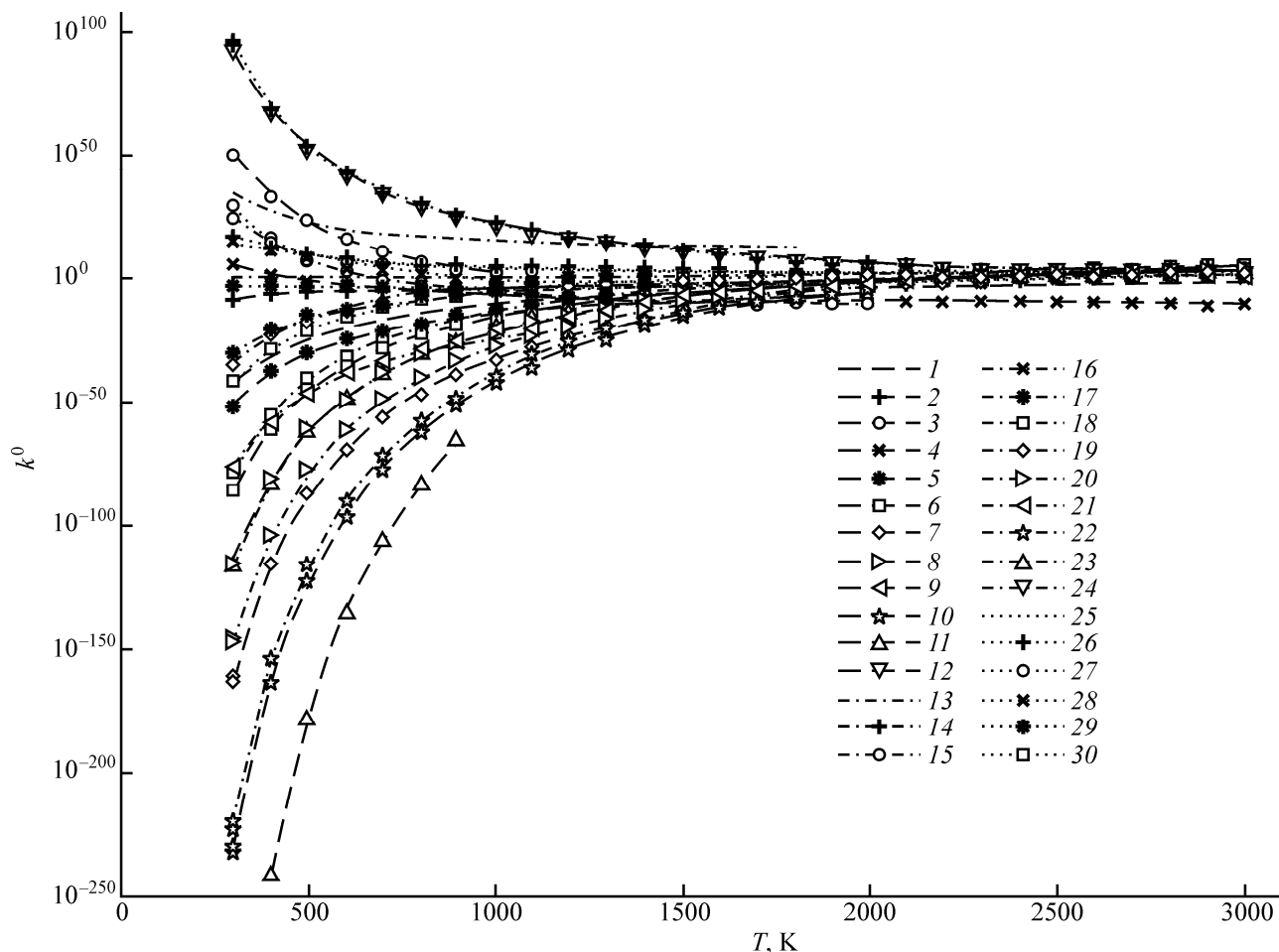
Fig. 6. Equilibrium constants of the reactions. (*1*) $N_2 + H_2 + 2C \rightarrow 2HCN$, (*2*) $2HCN \rightarrow (CN)_2 + H_2$, (*3*) $C + 2H_2 \rightarrow CH_4$, (*4*) $N_2 + 3H_2 \rightarrow 2NH_3$, (*5*) $2C + N_2 \rightarrow (CN)_2$, (*6*) $UO_2 + 2C + 1/2 N_2 \rightarrow UN + 2CO$, (*7*) $2UO_2 + 5C + N_2 + 2H_2 \rightarrow 2UN + 4CO + CH_4$, (*8*) $UO_2 + 3C \rightarrow UC + 2CO$, (*9*) $UO_2 + 4C \rightarrow UC_2 + 2CO$, (*10*) $2UO_2 + 7C \rightarrow U_2C_3 + 4CO$, (*11*) $U_3O_8 + 14C \rightarrow 3UC_2 + 8CO$, (*12*) $2U + N_2 \rightarrow 2UN$, (*13*) $U + 2C \rightarrow UC_2$, (*14*) $U + C \rightarrow UC$, (*15*) $2U + 3H_2 \rightarrow 2UH_3$, (*16*) $UC + UC_2 \rightarrow U_2C_3$, (*17*) $UN + 2C \rightarrow UC_2 + 1/2 N_2$, (*18*) $PuO_2 + 2C + 1/2 N_2 \rightarrow PuN + 2CO$, (*19*) $PuO_2 + 2HCN \rightarrow PuN + 2CO + H_2 + 1/2 N_2$, (*20*) $2PuO_2 + 5C + N_2 + 2H_2 \rightarrow 2PuN + 4CO + CH_4$, (*21*) $PuO_2 + 3H_2 \rightarrow PuH_2 + 2H_2O$, (*22*) $2PuO_2 + 7C \rightarrow Pu_2C_3 + 4CO$, (*23*) $PuO_2 + 3C \rightarrow PuC + 2CO$, (*24*) $PuO_2 + 4C \rightarrow PuC_2 + 2CO$, (*25*) $Pu + H_2 \rightarrow PuH_2$, (*26*) $2Pu + N_2 \rightarrow 2PuN$, (*27*) $2Pu + 3H_2 \rightarrow 2PuH_3$, (*28*) $PuC + PuC_2 \rightarrow Pu_2C_3$, (*29*) $PuH_2 + 1/2 H_2 \rightarrow PuH_3$, and (*30*) $UO_2 + 2HCN \rightarrow UN + 2CO + H_2 + 1/2 N_2$.

stant of the chemical reaction; hence, the diffusion will limit the process rate, and further heating will be inefficient.

The thermodynamic calculation of the reactions of molecular nitrogen with graphite demonstrated the possibility of the formation of gaseous carbon–nitrogen compounds in microamounts. The cyanogen formation reaction is the most thermodynamically favorable among these reactions. However, for this reaction also the equilibrium constant at 2000 K is of the order of 10^{-6}. The cyanogen microamounts formed can be consumed in the reaction with UO_2 (Fig. 7) and thus removed from the reaction zone.

Correspondingly, the positive driving force of the thermodynamically unfavorable cyanogen formation process will be maintained in such reactions. This, in turn, can ensure an additional mechanism of the carbon transport to UO_2 without graphite diffusion through the layer of the UN formed.

Greenhalgh [2] considered the possibility of preparing uranium and plutonium mononitrides from oxides in the presence of graphite in a flow of nitrogen with the addition of hydrogen. Thermodynamic analysis of the reactions of nitrogen, carbon, and hydrogen demonstrates the possibility of formation of HCN microamounts [reaction (I)]. The equilibrium constant of
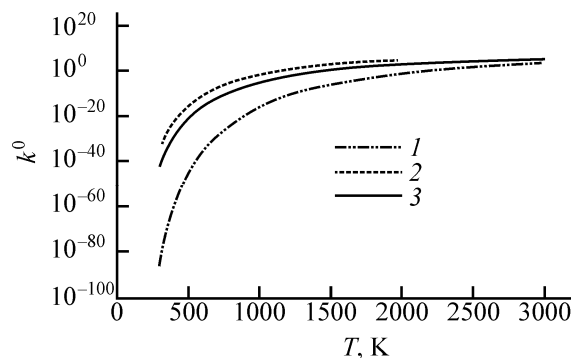
Fig. 7. Equilibrium constants of the (*1*) overall reaction of uranium monXonitride synthesis $UO_2 + 2C + 1/2 N_2 \rightarrow UN + 2CO$, (*2*) reaction of mononitride synthesis from cyanogen $UO_2 + (CN)_2 \rightarrow UN + 2CO + 1/2 N_2$, and (*3*) reaction of moninitride synthesis from hydrogen cyanide $UO_2 + 2HCN \rightarrow UN + 2CO + H_2 + 1/2 N_2$.

this process at 2000 K is of the order of 2×10^{-4}, being higher by two orders of magnitude than that of the $(CN)_2$ formation. The formation of HCN, as well as of $(CN)_2$, under such conditions is thermodynamically unfavorable, but HCN can also be removed from the reaction zone via reaction with UO_2 [reaction (IV)]. Thus, introduction of hydrogen into the system should ensure an additional mechanism of carbon transport, more efficient than via cyanogen formation without hydrogen. The corresponding behavior of the system in the presence of H_2 and without it was observed in [5].

Because the amount of gaseous reaction products in the mononitride formation reactions [(II), (III), (IV)] exceeds the amount of gaseous reactants, it can be anticipated that the reaction equilibrium can be shifted toward the products by decreasing the pressure in the system. However, a decrease in the concentration of the gaseous reactants, caused by a decrease in the pressure, will cause a decrease in the overall process rate and metallization of U and Pu [7].

Thus, using the HSC Chemistry 7.1 and TeDy programs, we studied the behavior of the physicochemical system characteristic of the carbothermal synthesis. We calculated the chemically equilibrium compositions of the system for the temperature range 1300–2000°C, pressure range 0.01–2 atm, and various nitrogen concentrations in the system. We performed thermodynamic evaluation of the possible reactions. The following conclusions can be made.

– Hydrogen cyanide can be formed in the presence of hydrogen. Hydrogen cyanide can accelerate the synthesis owing to the appearance of an additional mecha-

nism of the carbon transport to the reaction surface, which agrees with the experimental data described in [5].

– Cyanogen formation is possible at temperatures higher than 1400°C. Cyanogen can also ensure an additional mechanism of the carbon transport.

– Tendency to Pu and U metallization is observed at temperatures exceeding 1400 and 1600°C, respectively.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. Zabudko, L., Zozulya, D., Ivanov, Y., et al., Abstracts of Papers, *Int. Conf. on Fast Reactors and Related Fuel Cycles: Next Generation Nuclear Systems for Sustainable Development*, Yekaterinburg (Russian Federation), June 26–29, 2017, p. 57.

2. Greenhalgh, W.O., *J. Am. Ceram. Soc.*, 1973, vol. 56, pp. 553–557.

3. Roine, A., *HSC Chemistry 7.11*, Pori (Finland): Outotec, 2011. http:// www.outotec.com/hsc.

4. Pautasso, G., Richter, K., and Sari, C., *J. Nucl. Mater.*, 1988, vol. 158, pp. 12–18.

5. Bardelle, P. and Warin, D., *J. Nucl. Mater.*, 1992, vol. 188, pp. 36–42.

6. Arai, Y., Fukushima, S., Shiozawa, K., and Handa, M., *J. Nucl. Mater.*, 1989, vol. 168, pp. 280–289.

7. Kotel'nikov, R.B., Bashlykov, S.N., Kashtanov, A.I., and Men'shikova, T.S., *Vysokotemperaturnoe yadernoe toplivo* (High-Temperature Nuclear Fuel), Moscow: Atomizdat, 1978.

8. Muromura, T. and Tagawa, H., *J. Am. Ceram. Soc.*, 1978, vol. 61, nos. 1–2, pp. 30–35.

9. Ogawa, T., *J. Nucl. Mater.*, 1997, vol. 247, pp. 151–157.

10. Bochkareva, A.A., Shults, O.V., Peshkichev, I.V., et al., Abstracts of Papers, *5-ya Mezhdunarodnaya konferentsiya-shkola po khimicheskoi tekhnologii KhT'16: Satellitnaya konferentsiya XX Mendeleevskogo s''ezda po obshchei i prikladnoi khimii* (5th Int. Conf.-School on Chemical Technology CT'16: Satellite Conf. of XX Mendeleev Congr. on General and Applied Chemis-

try), May 16–20, 2016, Volgograd: Volgogradskii Gos. Tekh. Univ., 2016, vol. 2, pp. 370–372.

11. Bochkareva, A.A., Shults, O.V., Makeyeva, I.R., et al., in *Zababakhinskie nauchnye chteniya: Sbornik materialov XIII Mezhdunarodnoi konferentsii* (Zababakhin Scientific Readings: Coll. of Papers of XIII Int. Conf.), March 20–24, 2017, Snezhinsk: Vseross. Nauchno-Issled. Inst. Tekh. Fiziki, 2017, p. 244.

12. Bochkareva, A.A., Shults, O.V., Makeyeva, I.R., et al., Abstracts of Papers, *VII Mezhdunarodnyi simpozium "Khimiya i khimicheskoe obrazovanie"* (VII Int. Symp. "Chemistry and Chemical Education"), Oct. 17–20, 2017, Vladivostok: Dal'nevost. Fed. Univ., 2017, p. 57.

13. Peshkichev, I.V., Shults, O.V., Makeyeva, I.R., et al., Abstracts of Papers, *VII Mezhdunarodnyi simpozium "Khimiya i khimicheskoe obrazovanie"* (VII Int. Symp. "Chemistry and Chemical Education"), Oct. 17–20, 2017, Vladivostok: Dal'nevost. Fed. Univ., 2017, p. 89.

14. Peshkichev, I.V., Kuropatenko, V.F., Makeyeva, I.R., et al., *Vesnt. Yuzhnoural'sk. Gos. Univ., Ser. Mat. Model. Progr.*, 2018, vol. 11, no. 1, pp. 84–94. DOI: 10.14529/mmp180108.

15. Barin, I., *Thermochemical Data of Pure Substances*, Weinheim: VCH, 1995.

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