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Plasmachemical synthesis and evaluation of the thermal conductivity of metal-oxide compounds for prospective nuclear fuel

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Abstract. The article considers the possibility for direct plasma-chemical synthesis of metal-oxide compounds, containing inclusions of fissile material`s dioxide (uranium) and a matrix of beryllium oxide with a high thermal conductivity and a low cross section for the resonant absorption of neutrons from the optimal in composition water-organic nitrate solutions, including the organic component (alcohols, ketones). The results of calculations of the optimal compositions of such solutions are presented and the regimes of their plasma treatment providing direct plasma-chemical synthesis in the air plasma of metal-oxide compounds of the required composition are determined. The results of calculations of the thermal conductivity coefficients of these compositions, consisting of a continuous component (matrix), in which the inclusions from ceramics in the form of uranium dioxide are placed, are presented. The obtained calculated data are compared with the experimental results.

1. Introduction

Nuclear fuel (NF) of uranium dioxide enriched in isotope uranium-235 has a number of significant drawbacks: low thermal conductivity, high brittleness, a tendency to crack, short use cycle, limited resource of uranium-235 isotope, etc. [1-2]. This caused a slowdown in the development of nuclear energetics and led in recent years to abandon it in a number of countries.

A promising direction is the creation of dispersive NF, which is characterized by the absence of direct contacts between fuel particles due to their uniform distribution in the matrix and has the following advantages [2-8]: high thermal conductivity and mechanical properties, high burnup of fissile materials, radiation resistance and strength, localization of fission products in the fuel, etc.

The advantages of plasma-chemical synthesis of metal-oxide compounds (MOC) from optimal water-organic nitrate solutions (WONS) having a net calorific value of not less than 8.4 MJ/kg, should include [9-15]: low specific energy consumption, one-step process, high speed process, homogeneous distribution of phases with a given stoichiometric composition, the ability to actively influence on the size and morphology of particles.

The purpose of the article is to determine the possibility of direct synthesis of MOCs “UO_2 – BeO” from WONS in air plasma and to assess the impact of matrix content on MOC thermal conductivity. The following tasks were set: thermodynamic modelling of WONS plasma treatment; determination of WONS compositions; impact assessment of matrix content on MOC thermal conductivity; comparison of calculated and experimental data.

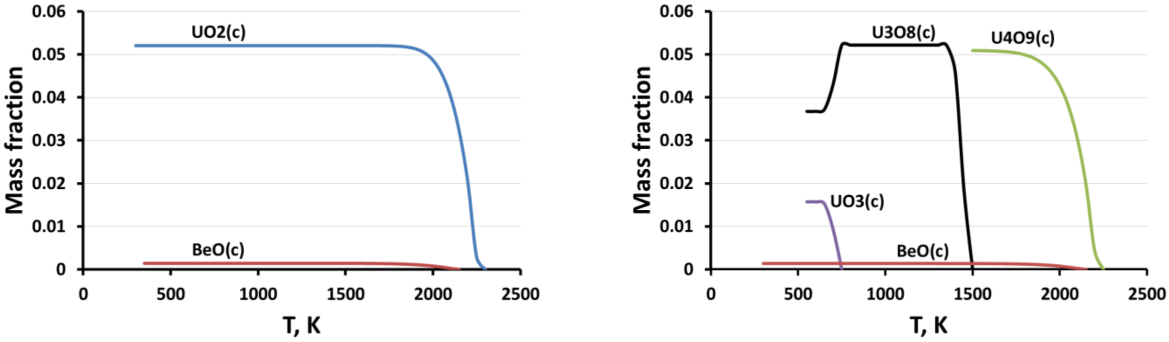
2. Thermodynamic analysis of the process of plasma-chemical synthesis of metal-oxide compounds

We obtained two compounds, MOC-1 and MOC-2, with the following WONS compositions:

- WONS-1 (27.3% H_2O – 34.6% $UO_2(NO_3)_2{\cdot}6H_2O$ – 34.0% C_2H_6O – 4.2% $Be(NO_3)_2{\cdot}4H_2O$) for MOC-1 “97.9% UO_2 – 2.1% BeO”;
- WONS-2 (29.4% H_2O – 37.2% $UO_2(NO_3)_2{\cdot}6H_2O$ – 29.0% C_3H_6O – 4.5% $Be(NO_3)_2{\cdot}4H_2O$) for MOC-1 “97.9 % UO_2 – 2.1% BeO”;
- WONS-3 (27.3% H_2O – 31.1% $UO_2(NO_3)_2{\cdot}6H_2O$ – 34.0% C_2H_6O – 7.6% $Be(NO_3)_2{\cdot}4H_2O$) for MOC-2 “95.8 % UO_2–4.2% BeO”;
- WONS-4 (29.4% H_2O – 33.4% $UO_2(NO_3)_2{\cdot}6H_2O$ – 29.0% C_3H_6O – 8.2% $Be(NO_3)_2{\cdot}4H_2O$) for MOC-2 “95.8 % UO_2–4.2% BeO”.

Thermodynamic calculations of the equilibrium compositions of WONS plasma processing products were carried out using licensed program for the thermodynamic calculation of the phase composition of arbitrary heterogeneous systems – TERRA software package. The calculations were carried out at atmospheric pressure (0.1 MPa) over a wide range of temperatures (300–4000 K) and changing values of initial mass fraction of air plasma coolant (air) 10–90 %.

Figure 1 shows the effect of temperature on the equilibrium compositions in the condensed phase of the main products of plasma treatment of ethanol`s based WONS-1 with the mass fraction of air 72 % (a) and 73 % (b).



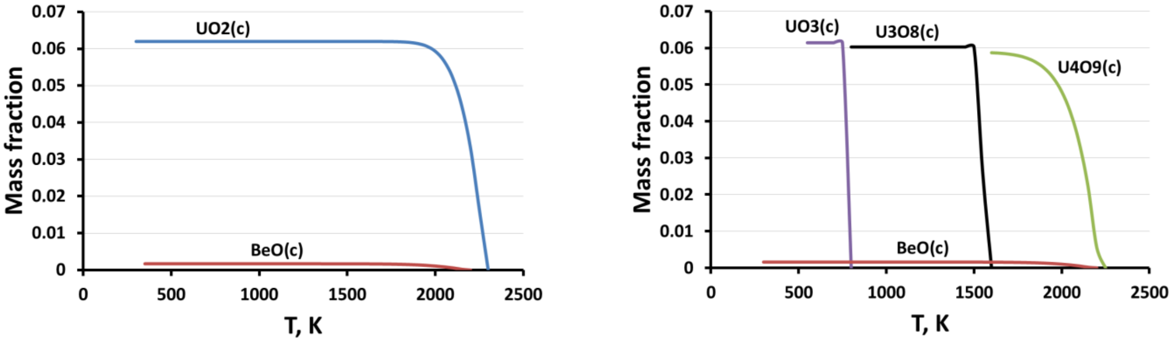
a) b)

Figure 1. Temperature effect on the equilibrium compositions in the condensed phase of the main products of plasma treatment of ethanol’s based WONS-1 with the mass fraction of air 72 % (a) and 73 % (b).

From the analysis of equilibrium compositions it follows that at a mass fraction of air of 72 % (figure 1a) in the temperature range 1000–1600 K, the required MOC-1 composition (97.9 % UO_2 – 2.1 % BeO) is formed in the condensed phase. An increase in the mass fraction of air from 72 % to 73 % (figure 1b) leads to composition “U_3O_8 – BeO” instead of required MOC-1.

Figure 2 shows the effect of temperature on the equilibrium compositions in the condensed phase of the main products of plasma treatment of acetone’s based WONS-2 with the mass fraction of air 69 % (a) и 71 % (b).

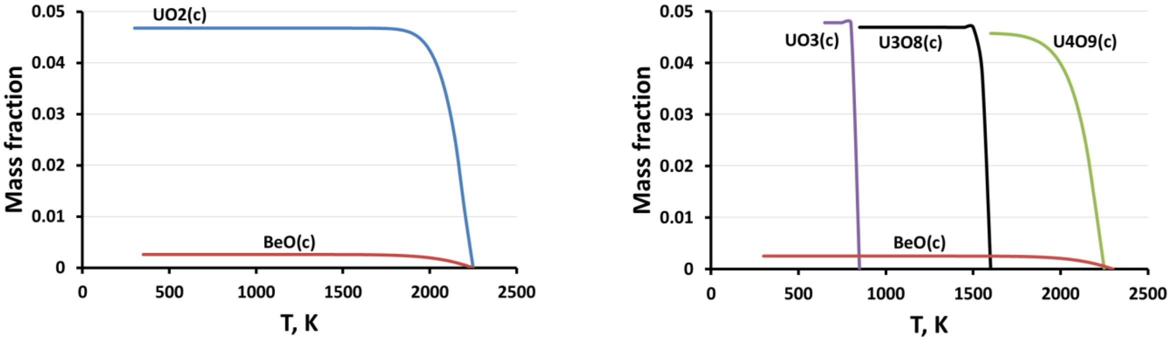
It can be seen that during plasma treatment of WONS-2 with a 69 % mass fraction of air (figure 2a), the required composition of MOC-1 (97.9 % UO_2 – 2.1 % BeO) is also formed in the temperature range 1000–1506 K. An increase in the mass fraction of air from 69 % to 71 % (figure 2b) leads to the formation of “U_3O_8 – BeO” composition in the condensed phase instead of required MOC-1. Replacement of ethanol with acetone does not change the composition of the main products of plasma treatment of WONS-2 in air plasma.



a) b)

Figure 2. Temperature effect on the equilibrium compositions in the condensed phase of the main products of plasma treatment of acetone`s based WONS-2 with the mass fraction of air 69 % (a) and 71 % (b).

Figure 3 shows the effect of temperature on the equilibrium compositions in the condensed phase of the main products of plasma treatment of ethanol`s based WONS-3 with the mass fraction of air 72 % (figure 3a) and 73 % (figure 3b).

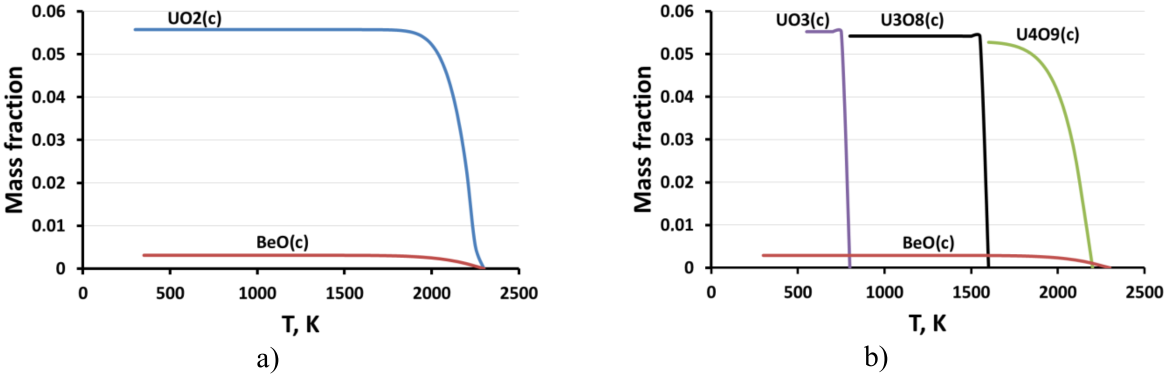


a) b)

Figure 3. Temperature effect on the equilibrium compositions in the condensed phase of the main products of plasma treatment of ethanol`s based WONS-3 with the mass fraction of air 72 % (a) and 73 % (b).

From the analysis of equilibrium compositions it follows that during plasma treatment of WONS-3 with mass fraction of air of 72 % (figure 3a) in the temperature range 1000–1600 K, the required MOC-2 composition (95.8 % UO_2 – 4.2 % BeO) is formed in the condensed phase. An increase in the mass fraction of air from 72 % to 73 % (figure 3b) leads to the formation of “U_3O_8 – BeO” composition in the condensed phase instead of required MOC-2.

Figure 4 shows the effect of temperature on the equilibrium compositions in the condensed phase of the main products of plasma treatment of acetone`s based WONS-4 with the mass fraction of air 69 % (a) and 71 % (b).



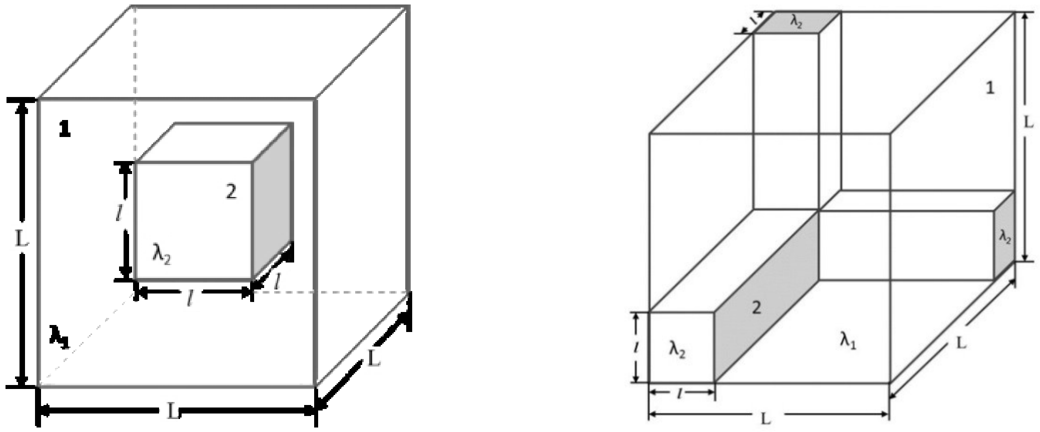
a) b)

Figure 4. Temperature effect on the equilibrium compositions in the condensed phase of the main products of plasma treatment of acetone`s based WONS-4 with the mass fraction of air 69 % (a) and 71 % (b).

From the analysis of equilibrium compositions it follows that during plasma treatment of WONS-4 on the basis of acetone with mass fraction of air of 69 % (Fig. 4a) in the temperature range 1000–1600 K, the required MOC-2 composition (95.8 % UO_2 – 4.2 % BeO) is formed in the condensed phase. An increase in the mass fraction of air from 69 % to 71 % (Fig. 4b) also leads to the formation of “U_3O_8 – BeO” composition in the condensed phase instead of required MOC-2.

3. Choice of the model for calculation of the coefficients of thermal conductivity of metal-oxide compounds “beryllium oxide-uranium dioxide”

To calculate the thermal conductivity λ of the composite material, an elementary cell was used (Fig. 5). The coefficient of thermal conductivity of a unit cell depends on the thermal conductivity λ_1 of the matrix material (BeO) and the thermal conductivity λ_2 of the inclusion material (UO_2). To effectively remove heat from the inclusion, it is necessary to satisfy the condition $\lambda_1 > \lambda_2$. Calculations of thermal conductivity coefficients were carried out at following values of L and l parameters: $300 \leq L \leq 600$ µm and $100 \leq l \leq 400$ µm [16].



a) b)

Figure 5. Elementary cells of metal-oxide composition “BeO–UO_2”: with inclusions (a) and with interpenetrative components (b), block 1 for matrix (BeO), block 2 for inclusion (UO_2).

Equations below are for calculation of thermal conductivity coefficient λ according to the various models. To describe closed inclusion model that implies split of unit cell with adiabatic (impenetrable for current streamlets) planes (IAS) the following equation (1) is used [17]:

$$\frac{\lambda}{\lambda_1}=\frac{v-(v-1)\cdot(1-m_2^{2/3})\cdot m_2^{1/3}}{v-m_2^{1/3}\cdot(v-1)}, \tag{1}$$

where m_2 is volume density of block 2 material and v is ratio of thermal conductivity coefficients; λ_2 and λ_1 could be expressed through equations:

$$m_2=\frac{V_2}{V_1}=\left(\frac{l}{L}\right)^3,\; v=\frac{\lambda_2}{\lambda_1},$$

where λ_1 and λ_2 are thermal conductivity coefficients of block 1 and block 2 materials respectively, L is block 1 size, l is block 2 size, V_1 is block 1 volume, V_2 is block 2 volume.

The equation (2) below is used to describe closed inclusion model that implies split of unit cell with isothermal (penetrable for current streamlets) planes (IIS) [17]:

$$\frac{\lambda}{\lambda_1}=\frac{1+(v-1)\cdot m_2^{2/3}}{1+(v-1)\cdot m_2^{2/3}\cdot(1-m_2^{1/3})}. \tag{2}$$

Based on Eiken results, Odelevsky V.I. [17], employed equation (3) to calculate the effective thermal conductivity of closed inclusion mixtures:

$$\frac{\lambda}{\lambda_1}=1-\frac{m_2}{\dfrac{1}{1-v}-\dfrac{1-m_2}{3}}. \tag{3}$$

Equation (3) describes Odelevsky closed inclusion model (Odel.) [18].

When investigating conductivity of various ordered structures with inclusions, it is necessary to mention findings obtained by Lichteneker, which describe two types of component structure: equal and unequal [13]. In the case of unequal structure the form of inclusion could be square or ellipsoidal (on a plane) and also parallelepipedic, spherical or ellipsoidal (in a space). Lichteneker defines notion of plate as plane boundary between two materials: matrix and inclusion. If heat flow is directed parallel to plate, then it is parallel orientation, and if heat flow is directed perpendicularly to plate, then it is perpendicular orientation [12].

Lichtenecker generalized conductivity model for mixtures with unequal components in case of parallel orientation of plates (LichtePAR) follows the formula (4) [17]:

$$\lambda_{//}=(1-m_2)\cdot\lambda_1+m_2\cdot\lambda_2. \tag{4}$$

To describe Lichtenecker generalized conductivity model for mixtures with unequal components in case of perpendicular orientation of plates (LichtePER) it is used the formula (5) [17]:

$$\lambda_{\perp}=\left(\frac{1-m_2}{\lambda_1}+\frac{m_2}{\lambda_2}\right)^{-1}. \tag{5}$$

Lichtenecker generalized conductivity model for mixtures with equal components having square form (Lichte2) follows the formula (6) [17]:

$$\lambda=\lambda_1^{1-m_2}\cdot\lambda_2^{m_2}. \tag{6}$$

In case if the mixture consists of three or more components, it should be applied the model for multicomponent mixtures following the formula (7) [17]:

$$\frac{\lambda}{\lambda_1}=\left\{\frac{m_2}{1-m_1}\left[1-\frac{1-m_1}{\dfrac{1}{1-v_{12}}-\dfrac{m_1}{3}}\right]+\frac{m_3}{1-m_1}\left[1-\frac{1-m_1}{\dfrac{1}{1-v_{13}}-\dfrac{m_1}{3}}\right]\right\}. \tag{7}$$

4. Results of the calculation of the coefficients of thermal conductivity of metal-oxide compounds “beryllium oxide-uranium dioxide” and their discussion

Figure 6 shows the effect of temperature on the thermal conductivity λ of the composite material in the form of MOC-1 (97.9 % UO_2 – 2.1 % BeO) and MOC-2 (95.8 % UO_2 – 4.2 % BeO).

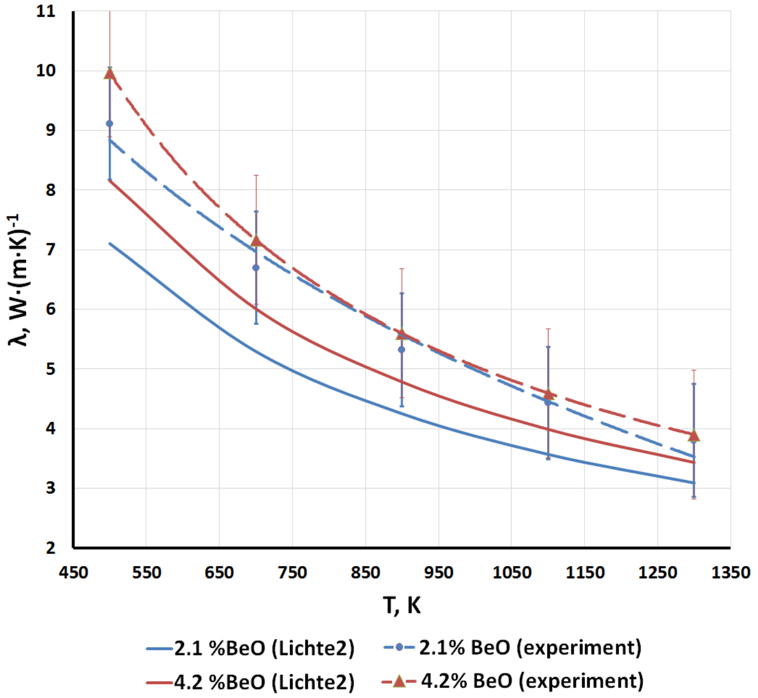


Figure 6. Effect of temperature on the coefficient of thermal conductivity λ of the composition material in the form of MOC-1 (97.9 % UO_2 – 2.1 % BeO) and MOC-2 (95.8 % UO_2 – 4.2 % BeO).

From the analysis of the obtained graphs (Fig. 6) it follows that as the temperature increases, the thermal conductivity of the MOC-1 (97.9 % UO_2 – 2.1 % BeO) and MOC-2 (95.8 % UO_2 – 4.2 % BeO) decreases.

5. Conclusion

As a result of the calculations optimum compositions of water-organic nitric solutions based on ethanol and acetone as well as the conditions (mass phase ratio, temperature) providing the plasma-chemical synthesis of MOC-1 (97.9 % UO_2 – 2.1 % BeO) and MOC-2 (95.8 % UO_2 – 4.2 % BeO) in air plasma were determined.

As a result of the calculations for thermal conductivity coefficients of the MOC-1 and MOC-2 with the use of a number of models it was shown that the Lichtenecker generalized conductivity model most accurately describes the experimental data.

All obtained results could be used in the production of various metal-oxide compounds for prospective nuclear fuel.

6. Acknowledgment

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