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Thermodynamic Analysis of Radioactive Graphite Oxidation in NiO-NaCl-KCl-Na_2CO_3-K_2CO_3 Melt in the Atmosphere of Argon

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Abstract

Behavior of U, Pu radionuclides was investigated when heating radioactive graphite in NaCl – KCl – Na_2CO_3 – K_2CO_3 melt with NiO additives using the thermodynamic modeling method. Calculations were made by the TERRA software that is used for the determination of phase composition, thermodynamic and transport properties, taking into account chemical and phase changes in temperature range 373 – 3273 K. Calculation of equilibrium phase composition and parameters of equilibrium was carried out using reference information about properties of the individual substances (INVATERMO, HSC, etc.). This study demonstrates that at a temperature of 1273 K the condensed carbon burns down with the formation of CO and CO_2. Increasing temperature to 1673 K causes the condensed compounds of uranium to evaporate. This study determined that uranium exists in the form of ionized UO_3^- in temperature range from 1673 to 3273 K. Plutonium exists in the form of gaseous PuO_2, PuO in temperature range 2373 – 3273 K.

Keywords: thermodynamic modeling, radionuclides, radioactive graphite.

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1. Introduction

Among all mass of the accumulated radioactive wastes (RW) graphite has a specific place. After the long radiation graphite doesn't gain any properties of it's useful application [1]. The total amount of the irradiated reactor graphite in Russia is about 55,000 tons. [2]. Besides Russia, the problem of treatment of the irradiated reactor graphite is relevant for Great Britain which has more than 77,000 tons, the USA – 50,000 tons and France – 23,000 tons [3]. The total amount of the irradiated graphite which is accumulated around the world is about 250,000 tons.

At present in the world there is no final decision on a problem of disposal of waste graphite [4]. The most perspective way of treatment of the waste graphite materials is combustion [1]. According to experts, combustion of waste graphite will result in the formation of radioactive wastes which are ready for the long-term burial of 1-2% from the initial graphite volume [1].

There are various ways of graphite combustion: traditional; in a fluidized bed; using plasma-chemical reactor; gasification with overheated steam (pyrolysis); in a melt of alkali metal carbonates in the presence of oxidizer; in a melt of one of alkali metal carbonates or their mixtures in the presence of lead oxide.

The aim of this research is the determination of equilibrium composition of gaseous phase at flameless oxidation of radioactive graphite in NiO-NaCl-KCl-Na_2CO_3-K_2CO_3 melt in the atmosphere of argon in a wide temperature range. The task of the study is carrying out thermodynamic model operation of the considered system.

2. Experimental Technique

Investigation of the behavior of U, Pu radionuclides accumulated in graphite from the nuclear reactor was carried out by thermodynamic modeling method in temperature range from 373 to 3273 K in NiO-NaCl-KCl-Na_2CO_3-K_2CO_3 melt in the atmosphere of argon. The thermodynamic modeling method was earlier successfully applied in chemistry and metallurgy [7–11]. Calculations were carried out by means of TERRA software that is used for determination of phase composition, thermodynamic and transport properties of systems taking into account chemical and phase changes. The background used in the software is given in works [5, 6]. The calculation of equilibrium phase composition and parameters of equilibrium is carried out using reference information about properties of the individual substances (INVATERMO, HSC, etc.).

Data on an original composition of radioactive graphite is taken from [12, 13] and presented in Table 1. Assumed forms of radionuclides existing in this system are given in Table 2.

3. Results and Discussion

Phase distribution of carbon is presented in Figure 1. Nickel oxide reacts with carbon forming Ni. In temperature range 373 – 573 K the content of condensed carbon decreases to ~47 %, Na_2CO_3 to ~22 %, but the content of CO_2 increases to ~30 % and K_2CO_3 to ~1 %. In temperature range 573 – 873 K the content of condensed

Table 1: The composition of the original system.

Phase:		Phase composition:	Content, % mass
Gaseous (62,5 % mass)		Ar	100
Condensed phase (37,5 % mass)	Oxide (15,6 % mass)	NiO	100
	Salt (18,7 % mass)	NaCl	25
		KCl	25
		Na_2CO_3	25
		K_2CO_3	25
	Radioactive graphite (3,2 % mass)	C	97,57022812
		U	2,341685475
		Pu	0,088086

Table 2: Assumed forms of radionuclides.

Radionuclide in graphite	Compound type in the equilibrium system
^{12}C, ^{14}C	$C_{(c)}$, $C_{(g)}$, $CO_{(g)}$, $CO_{2(g)}$, $C_2O_{(g)}$, $C_3O_{2(g)}$, $Ni_3C_{(c)}$, $NiCO_{3(c)}$, $ClCO_{(g)}$, CO^+, CO_2^+
^{238}U, ^{236}U, ^{235}U	$U_{(g)}$, $UO_{(g)}$, $UO_{2(c)}$, $UO_{2(g)}$, $UO_{3(c)}$, $UO_{3(g)}$, $U_3O_{8(c)}$, $U_4O_{9(c)}$, $UOCl_{(c)}$, $UO_2Cl_{2(c)}$, U^+, UO^+, UO_2^+, UO_2^-, UO_3^-
^{239}Pu, ^{240}Pu, ^{241}Pu, ^{242}Pu	$PuO_{2(c.)}$, $PuO_{2(v.)}$, $PuO_{(v.)}$, PuO^+

C decreases to ~32 %, Na_2CO_3 to ~20 %, CO_2 to ~17 %, but the content of K_2CO_3 increases to ~3 % and CO to ~28 %. In temperature range 873 – 1073 K the content of C decreases to ~16 %, CO_2 to ~1 %, Na_2CO_3 to ~19 %, but the content of CO increases to ~60 % and K_2CO_3 to ~4 %. In temperature range from 1073 to 1273 K the content of CO increases to ~84 % and the content of both C and CO_2 decreases to zero. At the same time the content of Na_2CO_3 reaches ~13 %, and K_2CO_3 – 3 %. In temperature range 1273 - 1573 K the content of CO_2 increases to ~31 % and the content of CO decreases to ~ 69 %, the content of both K_2CO_3 and Na_2CO_3 reaches zero. In temperature range from 1573 to 2373 K carbon exists in the form of CO ~ 69 % and CO_2 ~ 31 % in the system. In temperature range 2373 - 3273 K The content of gaseous CO decreases to ~ 8 % and the content of gaseous CO increases to ~ 92 %.

Phase distribution of uranium is presented in Figure 2. In temperature range 373 – 473 K U exists in the form of condensed UO_2Cl_2. In temperature range 473 – 573 K the content of UO_2Cl_2 decreases to ~ 24 % and the content of UO_2 increases to ~76 %. In temperature range 573 – 673 K the content of UO_2Cl_2 decreases to zero and the content of UO_2 increases to ~ 99 %, $NaUO_3$ to ~ 1 %. In temperature range from 673 to 973 K the content of UO_2 decreases to ~ 88 % and the content of $NaUO_3$ increases to ~ 12 %. In temperature range 973 – 1073 K the content of UO_2 decreases to ~72 % and the content of both $NaUO_3$ and Na_3UO_4 increases to ~ 26 % and 2 %, respectively.

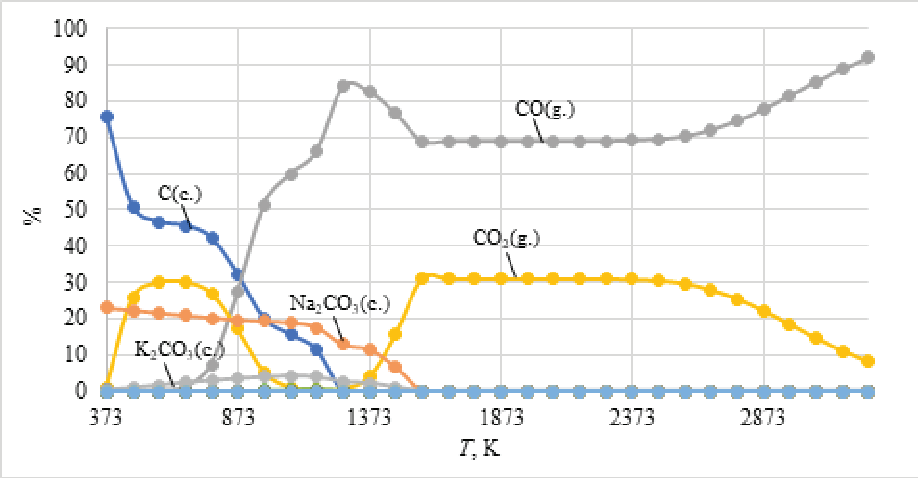

Figure 1: Phase distribution of carbon at combustion of radioactive graphite.

In temperature range from 1073 to 1273 K the content of UO_2 decreases to ~24 % and $NaUO_3$ to ~ 26 %, but the content of Na_3UO_4 increases to ~50 %. In temperature range 1273 – 1473 K the content of UO_2 tends to 12 % and Na_3UO_4 – 37 %, but the content of $NaUO_3$ increases to ~43 %, Na_2UO_4 to ~ 6 %, and ionized UO_3^- to 2 %. In temperature range from 1473 to 1673 K The content of UO_2, Na_3UO_4, $NaUO_3$, Na_2UO_4 decreases to zero and the content of UO_3^- reaches 100 %. In temperature range 1673 - 3273 K uranium exists in the form of ionized UO_3^-.

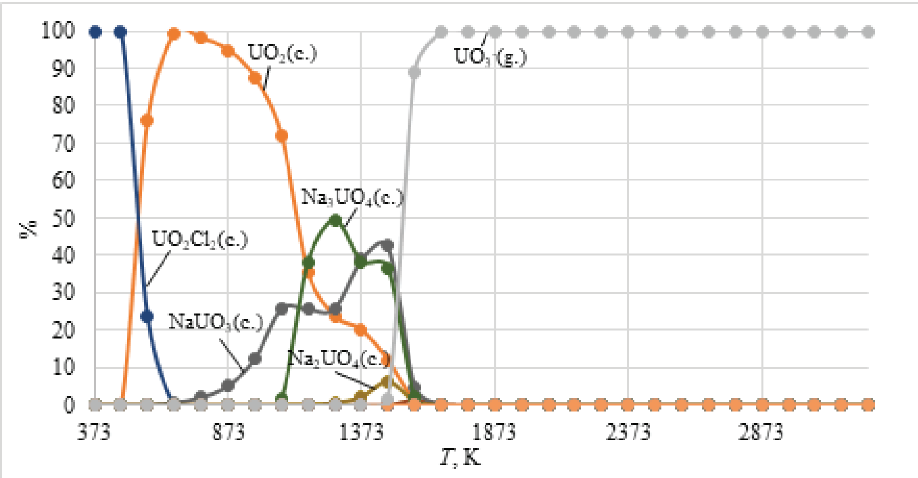

Figure 2: Phase distribution of uranium at combustion of radioactive graphite.

Phase distribution of plutonium is presented in Fig. 3. In temperature range 373 – 1873 K plutonium exists in the form of PuO_2. In temperature range from 1873 to 2173 K the content of condensed PuO_2 decreases to ~86 %, but the content of vaporized PuO_2 increases to ~14 %. In temperature range 2173 – 2373 K the content of condensed PuO_2 decreases to zero. At the same time the content of vaporized PuO_2 reaches 99 %, and vaporized PuO – 1 %. In temperature range from 2373 to 3273 K the content of vaporized PuO_2 decreases to ~88 % and the content of vaporized PuO increases to ~12 %.

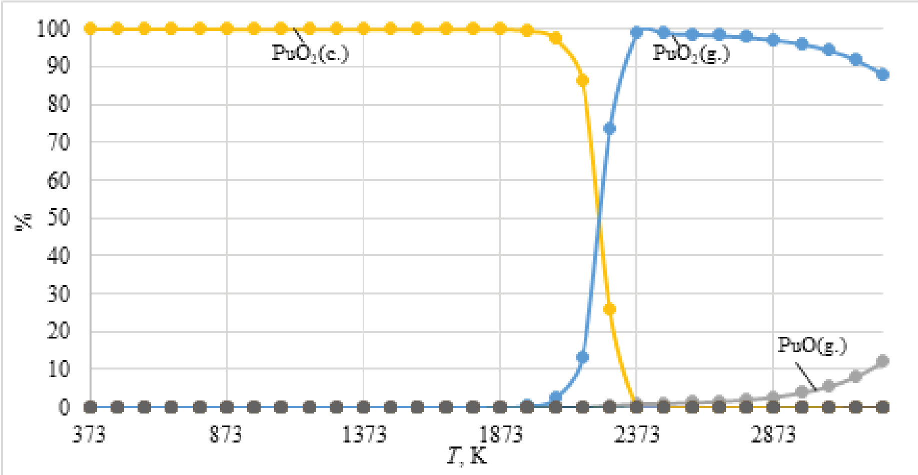

Figure 3: Phase distribution of plutonium at combustion of radioactive graphite.

4. Conclusion

Behavior of radionuclides is investigated by the thermodynamic modeling method at flameless oxidation of radioactive graphite in NiO-NaCl-KCl-Na_2CO_3-K_2CO_3 melt in the atmosphere of argon. By its results graphic dependences of phase distribution of radionuclides (U, Pu) are constructed. It is defined that at temperature of 1273 K the condensed carbon burns down with the formation of CO and CO_2. With the increasing temperature to 1673 K the condensed compounds of uranium evaporate. Heating of the system to temperature of 2373 K leads to the evaporation of condensed PuO_2. At 2373 K there is only a vapor-gaseous phase in the system.

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