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To cite this article: N Barbin *et al* 2020 *J. Phys.: Conf. Ser.* **1565** 012066

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Thermal characteristics of the radioactive graphite -CuO- Na₂CO₃-K₂CO₃-NaCl-KCl system in argon atmosphere

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Abstract. The article considers thermal characteristics of the radioactive graphite-CuO-Na₂CO₃-K₂CO₃-NaCl-KCl system in argon atmosphere. Thermodynamic calculations were carried out in the Terra program. Four temperature ranges with changes of thermal characteristics of the radioactive graphite-CuO-Na₂CO₃-K₂CO₃-NaCl-KCl system in argon atmosphere have been determined.

1. Introduction

The nuclear power engineering has almost unlimited fuel resources in contrast to traditional hydrocarbon power engineering.

Now there are three fundamental problems defining the societal attitudes to the development of nuclear power engineering as to potentially dangerous technology: risk of severe accidents, treatment of radioactive waste (including spent nuclear fuel), and non-proliferation of the fissionable materials (risk of global nuclear terrorism).

Among all stored radioactive wastes (RAW) graphite takes a specific place. After long radiation graphite doesn't gain any properties contributing to its useful application [1].

According to various estimates, the total amount of irradiated reactor graphite in Russia reaches 60 thousand tons. [2]. The problem of treatment of the irradiated reactor graphite is also relevant for Great Britain – more than 86 thousand tons, the USA – more than 55 thousand tons and France – more than 23 thousand tons [2]. The total amount of the stored irradiated graphite around the world is about 250 thousand tons.

At present there has been no final solution to the problem of waste graphite utilization in the world [2]. One of the options is its combustion [1].

Different ways of combustion of graphite are offered: traditional method, fluidized-bed combustion, the plasma-chemical reactor method, graphite gasification by superheated vapor (pyrolysis), combustion in a melt of alkali metal carbonates in the presence of oxidizer, and combustion in a melt of one of alkali metal carbonates or their mixtures in the presence of lead oxide.

The purpose of the study is to determine the thermophysical characteristics of the C-CuO-Na₂CO₃-K₂CO₃-NaCl-KCl-argon system in a wide temperature range.

The task of the work is to conduct computer simulation of the system in question.



2. Calculation procedure

Problems related to high-temperature processes play a significant role in numerous scientific studies. Carrying out full-scale experiments in these conditions does not always provide reliable data due to their complexity and errors of measurements. The computing experiment which serves to analyze states and processes is of particular importance. It also allows drawing conclusions about the investigated objects on the basis of model representation.

The model of thermodynamic equilibrium is often applied to study the complex of chemical composition systems under high temperatures. For realization of this model scientists G.V. Belov, B.G. Trusov developed the multi-purpose computer TERRA software. The theoretical foundation of the program is given in works [3, 4].

The method used is based on the principle of maximum entropy, which is valid in accordance with the second law of thermodynamics for any equilibrium system irrespective of the pathway by which the system reached the equilibrium, as in equation (1):

$$S = \sum_{i=1}^k S_i(p_i) \cdot n_i + \sum_{l=1}^L S_l \cdot n_l = \sum_{i=1}^k (S_i^0 - R_0 \cdot \ln \frac{R_0 \cdot T n_i}{v}) \cdot n_i + \sum_{l=1}^L S_l^0 \cdot n_l \quad (1)$$

where $S_i(p_i)$ is the entropy of i th component of the gas phase at a partial pressure $p_i = (R_0 T n_i)/v$; S_l is the entropy of l th condensed phase depending only on temperature; v is the specific volume of the whole system; and S_i^0 is the standard entropy of i th component of the gas phase at temperature T and pressure equal to 1 physical atmosphere.

Determination of the parameters of the equilibrium state consists in finding the values of all the dependent variables, including the numbers of moles of components and phases at which S reaches a maximum [5].

The set of phase components considered during each calculation is determined by the contents of the database of thermodynamic properties of individual substances. The database is based on information from systematized Russian and foreign reference manuals, as well as information collected over many years from specialized and periodicals. The database is quickly modified using the built-in utility program INFO. This program allows you to display the properties of any individual substance in graphical and tabular form. In addition, there are functions to delete, add, modify and restore [6,7].

Thermal characteristics of the radioactive graphite – CuO-Na₂CO₃-K₂CO₃-NaCl-KCl system in argon atmosphere are calculated by means of this program.

Thermodynamic modeling method was successfully applied in chemistry and metallurgy [8–10].

Conditions for thermodynamic modeling: a closed system in an argon atmosphere is considered; pressure – 0.1 MPa; temperature range 373 – 3273 K in increments of 100 K. Temperature change interval was 100 K. Phase composition: gas phase – 62.5% (Ar – 100% of mass), condensed phase – 37.5% (an oxide phase – 15.6% (CuO – 100% of mass), salt phase – 18.7% (Na₂CO₃ – 25% of mass, K₂CO₃ – 25% of mass, NaCl – 25% of mass, KCl – 25% of mass), radioactive graphite (C~97.57% of mass, U~2.34% of mass, Cl~0.035% of mass, Ca~0.050% of mass, Pu~0.001% of mass, Be~0.0002% of mass, Ni~0.0001% of mass, Cs~7.8 · 10⁻⁵% of mass, Sr~3.9 · 10⁻⁵% of mass, Am~0.0001% of mass, Eu~0.0001% of mass)).

3. Results and discussion

Figure 1 shows the change in system volume. At temperatures from 373 to 1173 K, the volume of the system increases to 1.74 m³/kg. At the temperature point of 1173 K, the inflection point is determined and at a temperature from 1173 to 1573 K, the volume of the system increases to 2.86 m³/kg. In the temperature range from 373 to 1173 K, an increase in the specific volume of the system from 0.52 to 1.74 m³/kg is observed. At a temperature of 1173 K, the inflection point is determined and an increase in the specific volume of the system from 1.74 to 2.86 m³/kg is traced in the temperature range from 1173 to 1573 K. At a temperature of 1573 K, the inflection point is determined, and in the temperature range from 1573 to 2373 K an increase in the specific volume of the system is observed from 2.86 to

4.72 m³/kg. At a temperature of 2373 K, the inflection point is determined, and in the temperature range from 2373 to 3273 K an increase in the specific volume of the system from 4.72 to 6.76 m³/kg is observed.

Figure 2 shows the change in the entropy of the system. In the temperature range from 373 to 1173 K, an increase in the entropy of the system from 3.1 to 4.17 kJ/(kg K) is observed. At a temperature of 1173 K, the inflection point is determined and in the temperature range from 1173 to 1573 K an increase in the entropy of the system from 4.17 to 4.93 kJ/(kg K) can be traced. At a temperature of 1573 K, the inflection point is determined, and in the temperature range from 1573 to 2373 K an increase in the entropy of the system is observed from 4.93 to 5.46 kJ/(kg K). At a temperature of 2373 K, the inflection point is determined and in the temperature range from 2373 to 3273 K an increase in the entropy of the system from 5.46 to 5.81 kJ/(kg K) can be observed.

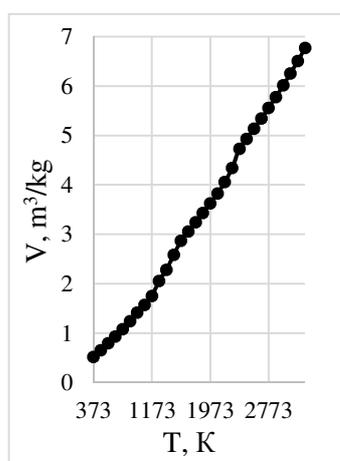


Figure 1. Change in the specific volume of the system C – CuO – Na₂CO₃ – K₂CO₃ – NaCl – KCl in argon atmosphere.

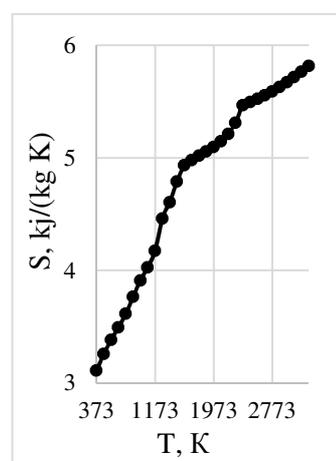


Figure 2. Change in the entropy of the C – CuO – Na₂CO₃ – K₂CO₃ – NaCl – KCl system in an argon atmosphere.

Figure 3 shows the change in the overall enthalpy of the system. In the temperature range from 373 to 1173 K, an increase in the total enthalpy of the system is observed from -1846.03 to -1016.83 kJ/kg. At a temperature of 1173 K, the inflection point is determined, and in the temperature range from 1173 to 1573 K an increase in the total enthalpy of the system from -1016.83 to 5.3 kJ/kg is observed. At a temperature of 1573 K, the inflection point is determined, and in the temperature range from 1573 to 2373 K an increase in the total enthalpy of the system is observed from 5.3 to 1119.19 kJ/kg. At a temperature of 2373 K, the inflection point is determined, and in the temperature range from 2373 to 3273 K an increase in the total enthalpy of the system from 1119.19 to 2119.32 kJ/kg is observed.

Figure 4 shows the change in the total internal energy of the system. In the temperature range from 373 to 1173 K, there is an increase in the total internal energy of the system from -1856.37 to -1147.29 kJ/kg. At a temperature of 1173 K, the inflection point is determined and in the temperature range from 1173 to 1573 K an increase in the total internal energy of the system from -1147.29 to -227.13 kJ/kg can be traced. At a temperature of 1573 K, the inflection point is determined, and in the temperature range from 1573 to 2373 K an increase in the total internal energy of the system is observed from -227.13 to 705.87 kJ/kg. At a temperature of 2373 K, the inflection point is determined and an increase in the total internal energy of the system from 705.87 to 1504.02 kJ/kg is observed in the temperature range from 2373 to 3273 K.

Figure 5 shows the change in the number of moles of system components. In the temperature range from 373 to 1173 K, the number of moles of system components is ~ 22.42 mol/kg. At a temperature of 1173 K, the inflection point is determined and an increase in the number of moles of system

components from 22.42 to 23.9 mol/kg is observed in the temperature range from 1173 to 1573 K. At a temperature of 1573 K, the inflection point is determined, and in the temperature range from 1573 to 2373 K, the number of moles of system components is ~ 23.9 mol/kg. At a temperature of 2373 K, the inflection point is determined, and in the temperature range from 2373 to 3273 K, an increase in the number of moles of system components from 23.9 to 24.87 mol/kg is observed.

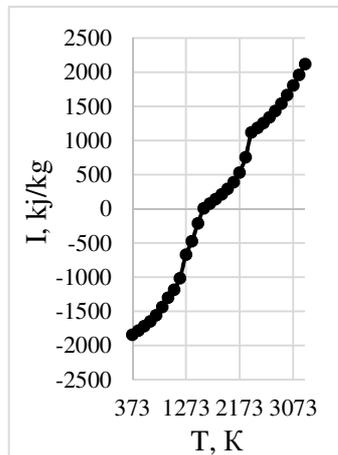


Figure 3. Change in the total enthalpy of the C – CuO – Na₂CO₃ – K₂CO₃ – NaCl – KCl system in an argon atmosphere.

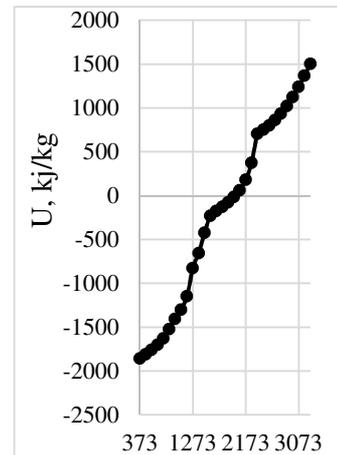


Figure 4. Change in the total internal energy of the C – CuO – Na₂CO₃ – K₂CO₃ – NaCl – KCl system in an argon atmosphere.

Figure 6 shows the change in the mass fraction of the condensed phases of the system. In the temperature range from 373 to 1173 K, a decrease in the mass fraction of the condensed phases of the system from 0.33 to 0.3 is observed. At a temperature of 1173 K, the inflection point is determined and a decrease in the mass fraction of the condensed phases of the system from 0.3 to 0.12 is observed in the temperature range from 1173 to 1573 K. At a temperature of 1573 K, the inflection point is determined, and in the temperature range from 1573 to 2373 K, a decrease in the mass fraction of the condensed phases of the system from 0.12 to 0 is observed.

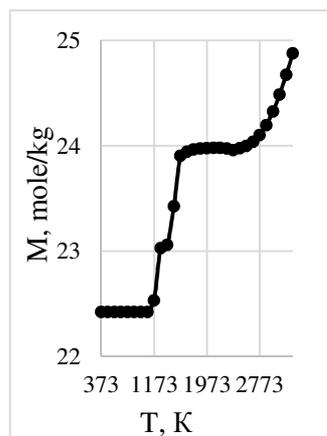


Figure 5. Change in the number of moles of the components of the C – CuO – Na₂CO₃ – K₂CO₃ – NaCl – KCl system in an argon atmosphere.

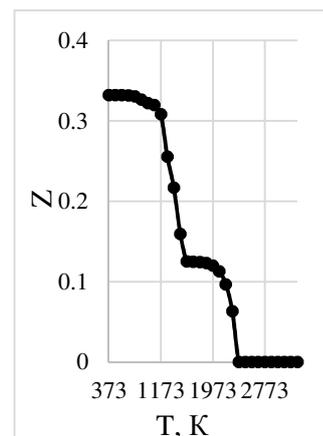


Figure 6. Change in the mass fraction of condensed phases of the C – CuO – Na₂CO₃ – K₂CO₃ – NaCl – KCl system in an argon atmosphere.

4. Conclusions

Changes of thermal properties of the complex system of radioactive graphite - $\text{CuO-Na}_2\text{CO}_3\text{-K}_2\text{CO}_3\text{-NaCl-KCl}$ depends on the physical and chemical processes. In temperature range of 373-1173 K sodium and potassium carbonates and chlorides and carbon prevail in the condensed phase. With temperature increase to 1573 K carbon burns in the reaction with an oxide-carbonate phase, and the condensed sodium and potassium carbonates and chlorides change into the gaseous phase. At temperature over 2373 K properties of the system depend on the processes proceeding in the gaseous phase.

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