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Immobilization of carbon-14 from reactor graphite waste by use of self-sustaining reaction in the C–Al–TiO_2 system

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Abstract

As a result of long-term neutron irradiation, the long-lived ^{14}C is produced in the reactor graphite. The exothermic self-sustaining reaction 3C(graphite) + 4Al + $3TiO_2$ = 3TiC + $2Al_2O_3$ was proposed for processing of such waste. In doing so, the carbon, including the ^{14}C, is chemically bound in the stable TiC. The reaction products in the C–Al–TiO_2 system were investigated both by thermodynamic simulation and experimentally in the course of this work.

At present, some countries commence the decommission of uranium–graphite reactors, which reached the operation term limit. During the operation period, reactor graphite waste has accumulated in these reactors in the form of fines and crumbs (bulk form). Because of long-term neutron irradiation, this waste contains significant amounts of long-lived radionuclide ^{14}C [1,2] which has a great potential hazard to human beings. The radionuclide ^{14}C has a half-life of 5730 years and is a biologically hazardous substance because of its readily assimilation by the human body [3]. For this reason, the processing of reactor graphite waste used for incineration with the exhaust of $^{14}CO_2$ into the atmosphere is ecologically unacceptable.

In Russia, an effective method of reactor graphite waste processing has recently been developed [4–6]. This method is based on the self-sustaining exothermic reaction.

$$3C(graphite) + 4Al + 3TiO_2 = 3TiC + 2Al_2O_3. \qquad (1)$$

In the course of this reaction, titanium oxide is reduced by aluminum, whereas the carbon, including the isotope ^{14}C inherent in graphite, is chemically attached to titanium resulting in chemically and thermally stable titanium carbide. This carbide bakes joint with corundum resulting in a low-porous ceramic matrix. For a complete understanding of graphite processing based on the above reaction, it was required to investigate areas of the non-stoichiometric reactions in the C–Al–TiO_2 system.

Thermodynamic analysis of the C–Al–TiO_2 system was performed using the software TERRA [7]. The phases C, Al, Al_2O_3, Al_4C_3, Al_4O_4C, Al_2OC, Ti, TiO, TiO_2, Ti_2O_3, Ti_3O_5, Ti_4O_7 and TiC were considered in the condensed state. The gaseous phase, consisting of Ar, C, C_2, C_3, O, O_2, CO, CO_2, C_2O, C_3O_2, Al, Al_2,

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Al_2O, Al_2O_2, Al_2O_3, AlC, AlC_2, Al_2C_2, Ti, TiO, TiO_2 species, were treated as ideal gas. Thermodynamic functions of substances being considered are taken from the reference books [8,9]. The unavailable thermodynamic functions of the solid and liquid aluminum oxicarbides Al_4O_4C and Al_2OC have been calculated [10].

The temperature maximum of 2327 K was calculated in the reacting C–Al–TiO_2 system that corresponds to the melting temperature of Al_2O_3. Thermodynamic calculation data on the equilibrium composition of condensed phase of reaction products in the C–Al–TiO_2 system have shown that the prohibitive aluminum carbide Al_4C_3 and undesirable oxicarbides Al_4O_4C and Al_2OC may be formed outside of the stoichiometric precursor's content. According to thermodynamic equilibrium, 0.16 wt.% of ^{14}C may be maximum release during the processing of the stoichiometric $3C + 4Al + 3TiO_2$ mixture in comparison with 100 wt.% by the incineration.

The calculated thermodynamic data were compared with experimental results. Premilled reactor graphite, standard pyrotechnic aluminum and titanium dioxide powder of commercial grade (or rutile concentrate) were used as source components. Preliminary batch compaction and hot compaction of the end product were thoroughly excluded. Mixture portions of 0.1–3 kg were incinerated in ceramic crucibles or in cylindrical metal containers. The experiments were conducted in argon atmosphere. The rate of self-sustaining reaction wave propagation in mixtures being investigated was measured as $\approx$1 mm/s. It should be pointed out that the self-sustaining reactions occur in a rather restricted area around the stoichiometric composition.

The reaction temperature measured in the stoichiometric $3C + 4Al + 3TiO_2$ mixture averages to 2300 ± 50 K that correlates well with calculated data. This temperature is favorable to the baking of titanium carbide and corundum produced. The end product was a porous cylinder, which took the shape and dimension of the crucible. The gas phase released during the process consisted of carbon oxides.

The specimens produced for a number of reacting batch formulations were analyzed by X-ray diffraction using Cu Kα radiation in the DRON-4 diffractometer. The phase composition of reaction products found experimentally agrees with that calculated within the accuracy of XRD analysis. At the same time, a detectable amount of non-stoichiometric titanium carbide TiC_y ($y < 1.0$) was found in the end product along with the stoichiometric TiC. This fact must be taken into account in the tailoring of batch formulations. Experimental results as a whole are evidence of thermodynamic equilibrium during the self-sustaining reaction. Some additional experimental findings for the C–Al–TiO_2 system are presented in [11,12].

The investigation performed has shown that, with the self-sustaining reaction technology proposed, ^{14}C is chemically strongly included into titanium carbide TiC.

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