

## PROCESSING OF GRAPHITE WITH CARBON-14 RETENTION

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### ABSTRACT

Waste graphite containing fragments of nuclear fuel and fission products is produced mainly as a result of operation of uranium-graphite reactors. Retention of radionuclides, including carbon-14, after disposal is an important goal of treatment procedure for such waste.

Conversion of waste graphite into a stable waste form acceptable for long term storage and disposal has been previously considered from a theoretical basis. A self-sustaining transformation process involving graphite mixed with suitable reaction precursors was proposed.

In the current study, such a self-sustaining process was studied both theoretically and experimentally in details. Three powdered reactant precursor mixtures were used: Al+SiO<sub>2</sub> (#1), Al+TiO<sub>2</sub> (#2), and Ti+SiO<sub>2</sub> (#3).

Numeric thermodynamic simulation was performed to determine equilibrium reaction temperatures and chemical compositions of the reaction products for a wide range of component ratios. The highest temperatures up to 2300 K were observed for precursor type #2. In contrast, reactions carried out using precursor type #3 demonstrated a minimal temperature rise of up to 1900 K.

Equilibrium phase composition diagrams were created for each precursor type. Regions of composition that exhibited complete binding of all chemical elements as well as production of stable final products were found to be rather narrow. Gas phase reaction products were studied to determine conditions that would minimize carry over of radionuclides. Carbon monoxide was shown to be the main gas phase component.

The behavior of radionuclides was studied for several possible processing schemes. For each precursor type, optimal processing regions were determined that provided complete carbon binding and minimized volatilization of radionuclides. About 8 – 13 wt.% of carbon could be successfully processed in the studied ranges of composition with the given precursors.

In the experimental studies, self-sustaining waste form synthesis processes were conducted in ceramic crucibles at ambient pressure in an air atmosphere. Batch masses used ranged between 0.1 – 1 kg. Best results were obtained for processing of graphite mixed with Al and TiO<sub>2</sub>. XRD analysis has shown titanium carbide and corundum in the waste form produced using this mixture. The experiments confirmed that carbon could be converted completely into a stable waste form.

## INTRODUCTION

Considerable amounts of high-level graphite waste containing fragments of fuel and fission products were accumulated during the operation of the uranium-graphite reactors. There is evidence that the  $^{14}\text{C}$ -content in reactor graphite may be as high as 1 wt.% (1). For safe disposal and long term storage, such wastes must be properly processed into chemically stable materials.

At present, known technologies for radioactive graphite processing are following:

1. Primarily, graphite incineration in an oxygen-containing atmosphere has been proposed (2). However, this method does not radionuclide immobilization in a stable waste form. Moreover, the  $^{14}\text{C}$  from the graphite is transferred to the gas phase as carbon dioxide. As a result, additional technological operations are required that extremely complicate the waste treatment process.
2. The U. S. Department of Energy Savannah River Technology Center has developed an immobilization process using a mixture of graphite fines with calcium fluoride ( $\text{CaF}_2$ , 15 wt.%) and plutonium oxide ( $\text{PuO}_2$ , 12 wt.%) (3). Heating the mixture at  $700\text{ }^\circ\text{C}$  with a sodium borosilicate glass frit results in a waste form acceptable for disposal. Evidently this process consumes external heat energy.
3. Recently, attempts were made to apply self-sustaining high-temperature synthesis (SHS) to graphite waste processing (4,5). SHS-reactions proceed in mixtures prepared by the addition of powdered metal fuel (aluminum or titanium) as an energy carrier and titanium or silicon dioxide to comminuted radioactive graphite waste:  $\text{C}(\text{graphite}) + \text{Al} + \text{SiO}_2$  (#1),  $\text{C}(\text{graphite}) + \text{Al} + \text{TiO}_2$  (#2),  $\text{C}(\text{graphite}) + \text{Ti} + \text{SiO}_2$  (#3).

When combustion of the mixture is initiated, metallothermic oxide reduction and interaction of the reduced elements with graphite occur. As a result, graphite is chemically bounded as stable metal carbides, which form a matrix for radionuclide oxide immobilization. High temperatures are developed from the metallothermic oxide reduction and carbide formation reactions. As a consequence, partial volatilization and dissociation of the reaction products occur, causing deviation from the stoichiometric equilibrium.

## THERMODYNAMIC SIMULATION OF THE THERMOCHEMICAL TREATMENT PARAMETERS

Thermodynamic simulation is, in essence, a numerical experiment and, at present, is widely used for prediction and analysis of the characteristics of high-temperature processes and reactions in multicomponent systems, including thermochemical treatment of radioactive waste (see, e.g., (6-10)). For thermodynamic simulation, the program ASTRA.4 (11) involving a database of thermodynamic characteristics of chemical compounds, comprising extensive Russian and foreign reference data (12-15), was used.

A detailed thermochemical analysis of reactions in reaction mixtures using mixtures #1 – #3 had been performed previously to determine reaction temperatures and phase compositions for the desired reaction products (16). It was shown that use of mixtures #2 provided the best results. Thus these mixtures were examined in detail.

In the thermodynamic calculations, formation of the following compounds due to reactions in reaction mixtures using mixtures #2 was considered: gas phase O, O<sub>2</sub>, C, C<sub>2</sub>, C<sub>3</sub>, CO, CO<sub>2</sub>, C<sub>2</sub>O, C<sub>2</sub>O<sub>3</sub>, Al, Al<sub>2</sub>, AlO, AlO<sub>2</sub>, Al<sub>2</sub>O, Al<sub>2</sub>O<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, AlC, AlC<sub>2</sub>, Al<sub>2</sub>C<sub>2</sub>, Ti, TiO, and TiO<sub>2</sub>, and condensed phase – C, Al, Al<sub>2</sub>O<sub>3</sub>, Al<sub>4</sub>C<sub>3</sub>, Ti, TiO, TiO<sub>2</sub>, Ti<sub>2</sub>O<sub>3</sub>, Ti<sub>3</sub>O<sub>5</sub>, Ti<sub>4</sub>O<sub>7</sub>, and TiC. The refined thermodynamic properties of titanium carbide were used in these calculations.

The calculation results are shown in Figures 1-3 as ternary diagrams.

Equilibrium reaction temperature as a function of mixture compositions is plotted in Fig. 1. A maximum temperatures of 2300 K and a very wide area of 2000 K are observed for mixtures #2 (Fig. 1a, b). It should be remembered that real temperatures in the reaction zone (where the aluminothermic process and carbide formation reaction occur) might far exceed (by few hundred degrees) the calculated equilibrium reaction temperatures. However, the real temperature might also be far below the calculated equilibrium temperature because of reaction incompleteness.

The equilibrium phase composition of the combustion products of Al-C-TiO<sub>2</sub> mixtures is shown on Fig. 2. As can be seen, the region of mixture formulations that allow formation of stable chemical compounds such as TiC, Al<sub>2</sub>O<sub>3</sub> and Ti<sub>x</sub>O<sub>y</sub> is rather wide (area 12 on the diagram). Area 12 is detailed on Fig. 2b, which shows also four subareas – 13, 14, 15 and 16. Only stoichiometric area 13 contains Al<sub>2</sub>O<sub>3</sub> and TiC with no titanium oxides.

The mixture formulations corresponding to diagram areas 1 - 11 are unsuitable for thermochemical treatment of graphite due to the presence of unbound C, Al, and Ti and easily hydrolyzed aluminium carbide, Al<sub>4</sub>C<sub>3</sub>, in the reaction end products.

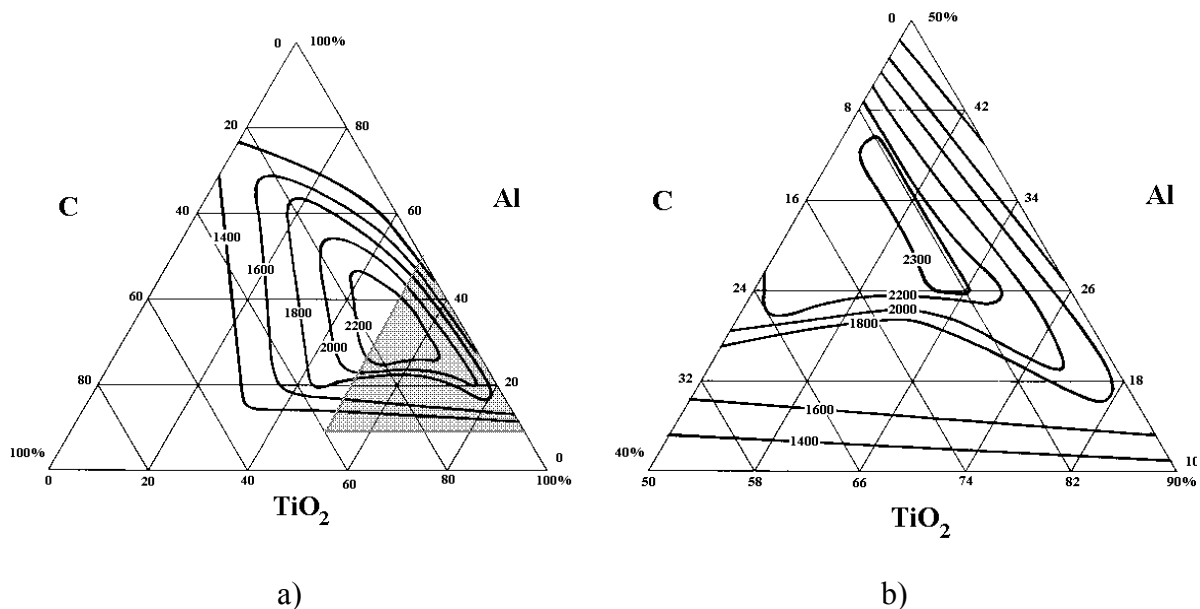


Fig.1. Isotherms of equilibrium temperature (K) in reacting mixtures Al-C-TiO<sub>2</sub> at pressure p=0.1 MPa.  
a) all mixtures, b) mixtures in the highlighted area on a).

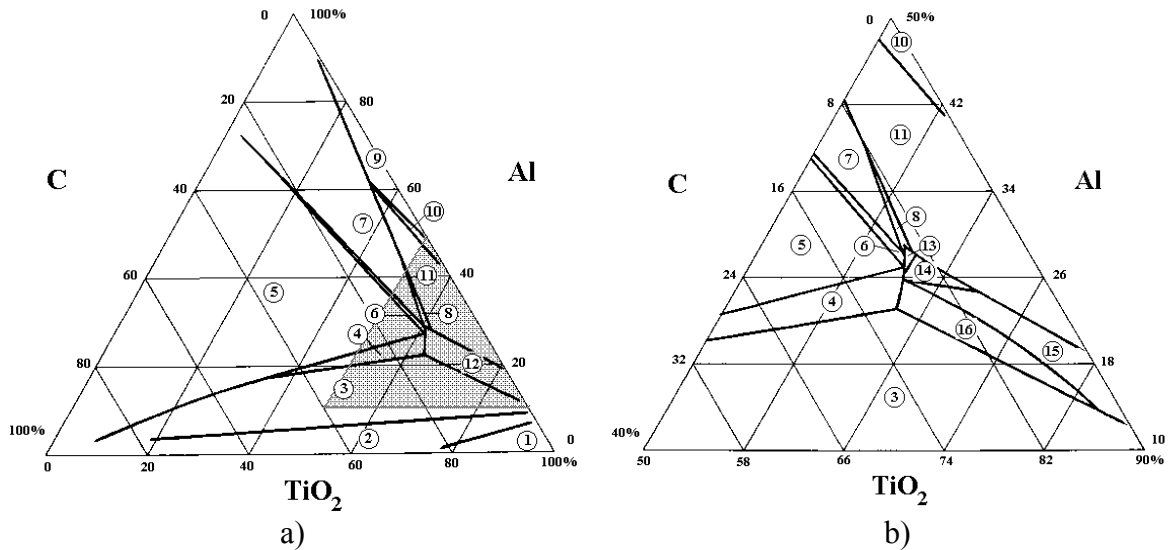


Fig.2. Equilibrium phase composition of condensed reaction products in reacting mixtures Al-C-TiO<sub>2</sub>.  
 a) – all mixtures, b) – mixtures in highlighted area on a).

*Phase areas:* 1 – C, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Ti<sub>4</sub>O<sub>7</sub>; 2 – C, Al<sub>2</sub>O<sub>3</sub>, Ti<sub>4</sub>O<sub>7</sub>, Ti<sub>2</sub>O<sub>3</sub>; 3 – C, Al<sub>2</sub>O<sub>3</sub>, Ti<sub>2</sub>O<sub>3</sub>, TiC; 4 – C, Al<sub>2</sub>O<sub>3</sub>, TiC; 5 – C, Al<sub>2</sub>O<sub>3</sub>, Al<sub>4</sub>C<sub>3</sub>, TiC; 6 – Al<sub>2</sub>O<sub>3</sub>, Al<sub>4</sub>C<sub>3</sub>, TiC; 7 – Al, Al<sub>2</sub>O<sub>3</sub>, Al<sub>4</sub>C<sub>3</sub>, TiC; 8 – Al, Al<sub>2</sub>O<sub>3</sub>, TiC; 9 – Al, Al<sub>2</sub>O<sub>3</sub>, Ti, TiC; 10 – Al, Al<sub>2</sub>O<sub>3</sub>, Ti, TiO, TiC; 11 – Al, Al<sub>2</sub>O<sub>3</sub>, TiO, TiC; 12 – Al<sub>2</sub>O<sub>3</sub>, Ti<sub>x</sub>O<sub>y</sub>, TiC; 13 – Al<sub>2</sub>O<sub>3</sub>, TiC; 14 – Al<sub>2</sub>O<sub>3</sub>, TiO, TiC; 15 – Al<sub>2</sub>O<sub>3</sub>, TiO, Ti<sub>2</sub>O<sub>3</sub>, TiC; 16 – Al<sub>2</sub>O<sub>3</sub>, Ti<sub>2</sub>O<sub>3</sub>, TiC.

It should be noted that one must not overlook the temperature conditions for a given mixture (Fig. 1) when using the calculation results for the phase composition corresponding to the desired end products. There could be a situation when the optimum (from the viewpoint of the best end product phase composition) mixture compositions would not react in a self-sustaining reaction due to the low equilibrium temperature.

For the reaction temperatures of 2000-2300 K, the main noncondensing components of the gas phase are carbon monoxide and carbon dioxide. Fig. 3 demonstrates the isolines of equilibrium concentrations of carbon monoxide (a) and dioxide (b) in the gas phase reaction products for reaction mixtures based on mixtures #2. The CO<sub>2</sub> content is always a few orders of magnitude lower than the CO content. The concentrations of CO and CO<sub>2</sub> are given on Fig. 3 in kg per kg of total combustion products mixture (gas and condensed phases).

Comparison of the Fig. 2 and Fig. 3 data shows that for the most interesting areas of the phase diagrams with respect to end product composition, the CO content approaches 0.01 kg/kg (Fig. 3a). And thus, in view of (1), <sup>14</sup>CO and <sup>14</sup>CO<sub>2</sub> releases can reach 10<sup>-3</sup> and 10<sup>-7</sup> kg/kg of batch materials respectively.

The Table presents the overall equilibrium composition for the reaction products for Al-C-TiO<sub>2</sub> mixtures in regions 3 – 16 of Fig. 2a, and 2b.

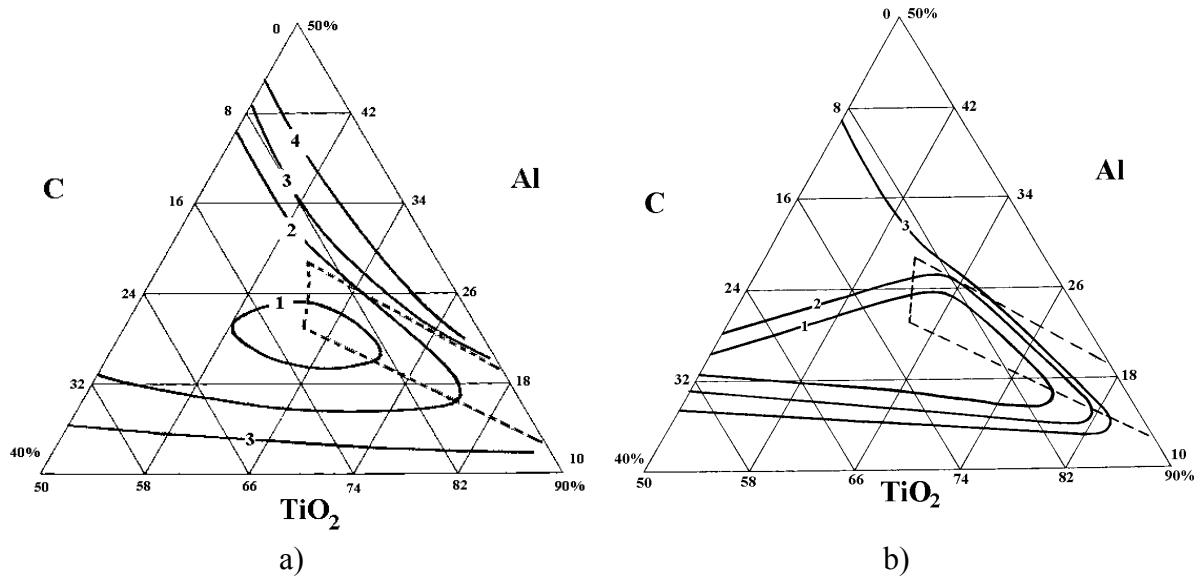


Fig. 3. Isocurves of carbon monoxide (a) and carbon dioxide (b) at equilibrium concentration in reacting mixtures Al-C-TiO<sub>2</sub>. (Dashed lines correspond to the outline of area 12 on Fig. 2a). The numbers denote concentrations - on Fig. 3a: 1 –  $0.5 \cdot 10^{-1}$ , 2 –  $10^{-2}$ , 3 –  $10^{-5}$ , 4 –  $10^{-8}$  kg of CO/kg; - on Fig. 3b: 1 –  $10^{-5}$ , 2 –  $10^{-6}$ , 3 –  $10^{-7}$  kg of CO<sub>2</sub>/kg.

## EXPERIMENT

We did not aim to perform complete experimental studies, however, we carried out some tests on mixtures #1 - #3. For test simplification, we thoroughly excluded the preliminary batch compaction and hot compaction of the end product from the sum total of mechanical operations.

Standard graphite, aluminum, titanium, titanium dioxide and silicon dioxide powders were used as source components. Mixing was performed manually. Mixture portions of 0.1 – 1.0 kg were incinerated in a ceramic crucible. Special precautions were not applied to exclude the effects of ambient air.

**Table**  
Equilibrium composition of combustion products of Al-C-TiO<sub>2</sub> mixtures in regions 3 – 16 of Fig. 2

Constituent	Phase diagram region on Fig. 2b											
	3	4	5	6	7	8	10	11	13	14	15	16
	Source contents in Al/C/TiO <sub>2</sub> batch (wt. %)											
	20/15/65	25/15/60	30/15/55	34/10/56	45/10/45	32/9/59	50/2/48	30/6/64	28/10/62	26/10/64	24/8/68	24/12/64
Noncondensing gas phase mass fractions												
CO	5.42E-2	3.27E-2	1.75E-2	1.08E-2	1.11E-4	3.04E-3		2.93E-7	1.58E-2	2.64E-2	1.78E-2	6.32E-2
CO <sub>2</sub>	1.78E-5	5.51E-7	1.98E-7	1.17E-7	5.41E-10	3.93E-8			2.63E-7	5.66E-6	4.89E-6	1.91E-5
Condensing gas phase mass fractions												
Al		1.69E-4	5.61E-4	1.32E-3	2.56E-5	6.45E-4	1.74E-9	2.34E-5	1.28E-3	2.93E-5	1.12E-6	1.95E-8
Al <sub>2</sub>		2.13E-7	2.91E-6	1.35E-5	1.77E-7	7.16E-6		1.66E-7	9.70E-6	4.77E-9		
AlO		6.39E-8	1.45E-7	3.34E-7	2.78E-9	1.96E-7		2.67E-9	5.00E-7	1.48E-7	6.85E-9	
Al <sub>2</sub> O		1.33E-3	7.17E-3	2.13E-2	3.53E-4	1.08E-2	3.44E-9	3.27E-4	1.89E-2	1.20E-4	2.06E-6	8.22E-9
Al <sub>2</sub> O <sub>2</sub>		1.27E-8	4.34E-8	1.39E-7	9.75E-10	8.42E-8		9.47E-10	1.89E-7	1.55E-8		
AlC		6.82E-10	3.75E-9	7.04E-9		2.26E-9			6.22E-9			
AlC <sub>2</sub>		1.02E-8	5.60E-8	5.70E-8		9.68E-9			3.72E-8			
Al <sub>2</sub> C <sub>2</sub>		6.14E-7	9.18E-6	1.35E-5	9.14E-8	2.09E-6			5.50E-6			
Ti		2.21E-9	3.53E-9	1.30E-8		1.47E-8		4.27E-8	3.05E-8	2.67E-7	1.52E-8	
TiO		3.48E-9	2.98E-9	8.91E-9		1.09E-8		2.07E-8	2.91E-8	3.29E-6	4.08E-7	1.78E-8
TiO <sub>2</sub>											2.52E-8	2.40E-9
Condensed phase mass fractions												
C	5.47E-2	4.57E-2	4.00E-2									
Al				4.89E-2	1.50E-1	5.00E-2	3.39E-1	6.58E-2				
Ti							6.04E-2					
Al <sub>2</sub> O <sub>3</sub>	3.78E-1	4.70E-1	4.43E-1	4.53E-1	3.82E-1	4.92E-1	3.03E-1	4.41E-1	4.99E-1	4.91E-1	4.53E-1	4.53E-1
TiO							1.97E-1	1.92E-1		4.01E-2	8.82E-2	
Ti <sub>2</sub> O <sub>3</sub>	1.54E-1										7.95E-2	2.00E-2
TiC	3.59E-1	4.49E-1	4.12E-1	4.19E-1		4.42E-1	9.97E-2	2.99E-1	4.64E-1	4.42E-1	3.60E-1	4.63E-1
Al <sub>4</sub> C <sub>3</sub>			7.90E-2	4.47E-2	1.29E-1							

Under such conditions, we could not achieve stable and complete combustion of Al-C-SiO<sub>2</sub> mixtures. The reaction ceased a few seconds after the initiator burnout that proceeds on the surface of the source mixture.

The combustion of Ti-C-SiO<sub>2</sub> mixtures ran better. The whole mixture continued to glow for a few minutes after initiator burnout.

However, the best results were achieved for Al-C-TiO<sub>2</sub>. In this case the end product was a porous cylinder which took the shape of the crucible. According to XRD data, the reaction products of a mixture composed of Al – 28, C – 9.5 and TiO<sub>2</sub> – 62.5 wt.% (area 14 on Fig. 2b) consist of titanium carbide, alumina and titanium oxide (Fig. 4a). The same mixture, but with some excess of graphite (corresponding to area 4 on Fig. 2b), was tested to make sure that all graphite in the area 14 mixtures is chemically bound. The appropriate XRD data are presented on Fig. 4b, which shows the clearly defined graphite peak not present on Fig. 4a. This data agrees with the results of the thermodynamic simulation (see Fig. 2b).

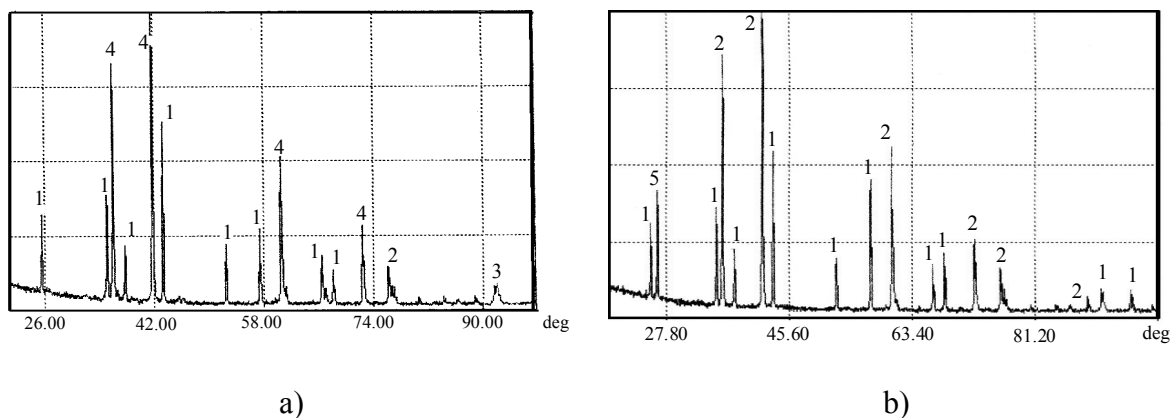


Fig. 4. XRD-analysis data for end reaction products of Al-C-TiO<sub>2</sub> mixtures.  
1 – Al<sub>2</sub>O<sub>3</sub>, 2 – TiC, 3 – TiO, 4 – TiC, TiO, 5 - C(graphite).

## CONCLUSIONS

Using numerical thermodynamic simulation:

- The reactions that convert graphite into chemically stable compounds (titanium and silicon carbides) were studied;
- The temperature ranges that support the most effective carbide-formation reactions were established in ternary diagrams of the source mixtures;
- In the ternary diagrams for the source mixtures, areas were established that are characterized by complete chemical binding of graphite and by the absence of unstable compounds in the end products;
- It was established that, under conditions of high reaction temperatures, certain source mixtures produce some amounts of undesirable carbon monoxide.

In conclusion, it would not be out of place to make the following remark. When thermodynamic simulation data are treated analytically, one must bear in mind that the higher is the process temperature and the longer is the process duration, the closer the calculation results will be to reality

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