Interaction of components features of the reaction mixture
\(\text{ZrO}_2(\text{m})-\text{Al}-\text{C}\) systems when heated

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Abstract. By the complex analysis basis of the interaction theory of the reaction mixture components \(\text{ZrO}_2(\text{m})-\text{Al}-\text{C}\) when heated to temperatures of 1650–1775°C and experimental data (DTA, x-ray diffraction analysis), the nature of the formation of final synthesis products is studied. The probability of multistage interaction of components in the heating process with the formation of aluminum oxide \(\text{Al}_2\text{O}_3\) and zirconium carbide \(\text{ZrC}\) as final components, which is accompanied by an intermediate stage of formation of intermetallic based on \(\text{Al}\) and \(\text{Zr}\), is noted. The results obtained indicate that it is advisable to further study the laws of phase and structure formation of materials in the considered system in order to obtain high-density functional ceramics of the oxide-carbide type.

1. Introduction

The reaction synthesis of many types of ceramic materials can significantly improve the manufacturability of products of various uses. The types of tool ceramics that have a set of properties that allow it to be used as the basis of a metal-cutting tool that can work at high cutting speeds were made and invented by the authors of the work [1–2]. The characteristics of such materials directly depend on the properties of their components formed during the chemical interaction of the components of the initial charge. The structure of tool ceramic usually consists of oxides, carbides, nitrides, and other high-hardness and high strength compounds. Known types of oxide-carbide ceramics for tool use mainly contain aluminum oxide, reinforced with dispersed particles of carbides, as well as zirconium oxide, which exhibits transformational hardening [3]. It is advisable to start creating ceramics of new compositions in order to increase productivity and reduce the energy intensity of synthesis processes by predicting the possibility of interaction of the components of the initial reaction mixtures. In this regard, it is of scientific interest to study the kinetics of the interaction of components of a reaction mixture of the composition \(\text{ZrO}_2(\text{m})-\text{Al}-\text{C}\), which, by analogy with the reaction of titanium oxide with aluminum and carbon [4–7], can be generally represented as:

\[
3\text{ZrO}_2(\text{m}) + 4\text{Al} + 3\text{C} \rightarrow 3\text{ZrC} + 2\text{Al}_2\text{O}_3. \tag{1}
\]

Such studies become even more relevant when the synthesis of the material is carried out using energy-intensive technologies, in particular — hot pressing, which is the most common method for producing ceramics, including instrumental purposes.
The purpose of this work is to establish the kinetics of the interaction of components of the reaction mixture ZrO$_2$(m)–Al–C during heating and to identify the possibility of using this system to produce ceramics of the oxide-carbide type for instrumental purposes, based on the analysis of the results of thermodynamic calculations, differential thermal and x-ray structural analyses.

2. Methods of study

The material test samples were prepared using a powder mixture which consists of zirconium dioxide of monoclinic production from SRPE «Tsirkonii» (Dneprodzerzhinsk, Ukraine), aluminum powder, and lampblack (table 1).

| Material                           | Technical conditions and standards |
|-----------------------------------|-----------------------------------|
| Zirconium dioxide powder (monoclinic) | TU–6–09–24–86                     |
|                                   | TUU 14–10–098–99                  |
| Aluminum powder PAP-4             | GOST 5494–71                      |
| Lampblack powder S-1              | GOST 18307–78                     |

The results of differential thermal analysis (DTA) were obtained on a high-temperature differential thermal analyzer HDTA–7, designed for the study of refractory materials in the temperature range of 20-2500 °C. The temperature rise is performed automatically according to a specified program with simultaneous registration of measurement results in coordinates: sample temperature – the temperature difference between the sample and the standard.

X-ray diffraction studies were performed using the DRON-2 diffractometer. Scanning of samples subjected to differential thermal analysis was performed in CuKα-radiation with a Ni filter.

The opportunity of reactions in the temperature range 100–1775 °C, taking place in a specified system, was established based on the calculation results of Gibbs free energy (ΔG). Thermodynamic quantities used in the calculations are taken from sources [8–11].

3. Discussion of results

According to the calculations, the values of the Gibbs energy change for the reaction (1) in the temperature range of 100–1700 °C are in the range of 13.8–225.6 kJ/mol. This indicates that the reaction being tested should not take place. However, we should consider the possibility of passing other chemical reactions between the components of the mixture.

According to the aluminum-carbon state diagram [12], the only stable compound formed in system (2) is Al$_4$C$_3$ carbide, which is released as a result of a peritectic reaction at 2300°C. At lower temperatures, the solubility of carbon in aluminum is extremely small: 0.14% (wt %) at 1000°C and 0.32 (wt %) at 1200°C.

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The results of thermodynamic calculations obtained for the equilibrium equation:

\[
\text{ZrO}_2 + 3\text{C} \rightarrow \text{ZrC} + 2\text{CO}
\]
characterize the interaction in the system (3). The change in the Gibbs energy in the temperature range of 100–1700°C, according to the calculations, is in the range of $-341.9$–$-64.7$ kJ/mol and indicates the possibility of passing this chemical reaction. The obtained data correlate well with the data [13], where it is also noted, that the temperature of the beginning of the interaction between ZrO$_2$ and C by the reaction (5) is 1400 °C. It is also known, that one of the methods of industrial synthesis of ZrC in large quantities is the carburization of a metal zirconium powder [14–16]. This may be possible as a result of the release of Zr in the reaction:

$$3\text{ZrO}_2 + 4\text{Al} \rightarrow 3\text{Zr} + 2\text{Al}_2\text{O}_3.$$  \hspace{1cm} (6)

The lower position of zirconium dioxide compared to aluminum oxide in the diagram of oxygen affinity for metals presented in [17] suggests, that such an interaction may take place. The presence of such interaction is also stated in the work [18]. These data are confirmed by DTA results (fig. 1) and x-ray diffraction analysis (fig. 2), taken from a sample obtained from a mixture of ZrO$_2$–22Al (wt %) (stoichiometric composition calculated from the equilibrium equation (7)). The first endothermic effect (652–685°C) on the DTA-thermograms (see fig. 1) corresponds to the melting of aluminum. Next, the Al melt begins to interact with zirconium oxide by reaction (7), which indicates itself as an exothermic effect at 770°C. The formed aluminum oxide (see the reaction (7)), in accordance with the results described in [19], has the structure $\theta$-$\text{Al}_2\text{O}_3$ at this temperature. Subsequently, at 1275 °C (see fig. 1), aluminum oxide will undergo polymorphic transformation into the $\alpha$-phase, which is stable for normal conditions.

![Figure 1. DTA-thermogram, obtained by heating and cooling a sample from a mixture of ZrO$_2$(m) – 22Al (wt %).](image)

Since we are dealing with a powder system, there is a possibility, that not all aluminum is involved in the zirconium release reaction. The part of aluminum that is on the border with zirconium released during the reaction (6) interacts with it to form intermetallics. This interaction corresponds to the peak of the DTA-diagram at 837°C.
The presence of zirconium dioxide peaks on the roentgenogram taken from the test sample (see fig. 2) indicates the presence in the composition of the material of the part, which did not react with Al, since before this aluminum was partially spent on the formation of intermetallides.

In [20] an assumption is made about the possibility of formation of an Al₇Zr₅ compound in this system with subsequent decay reaction:

$$\text{Al}_7\text{Zr}_5 \rightarrow \text{Zr}_2\text{Al} + \text{Zr}_3\text{Al}_2$$

(7)

Figure 2. X-ray diffraction pattern taken from a sample of ZrO₂(m) – 22Al (wt %) composition after heating in a DTA-analyzer.

At the same time, the authors of [21], who studied the interaction of zirconium with aluminum, found the presence of two intermetallides Al₃Zr and Al₂Zr in the final composition of the material along with other components. The possibility of formation of any of the above compounds should be related with the concentration of aluminum in the initial composition of the powder mixture in combination with temperature conditions. Many exo-and endoeffects that appear when heated above 1500 °C are probably the consequences of recrystallization of previously formed intermetallides, which eventually led to the formation of a stable phase of Al₂Zr, found in the composition of the final material as a result of x-ray diffraction studies (see fig. 2). Some of the temperature effects occurring in the range of 1500→1652→1350 °C may also indicate possible polymorphic transformations characteristic of previously formed oxides.

With the appearance of carbon in the reaction mixture (ZrO₂(m)–21Al–7C (wt %) – stoichiometric composition calculated by equation (1)), the exoeffect on the DTA-diagram related with the formation of intermetallides shifts to the right (peak at 915 °C in fig. 3).

At the same time, the temperature of the assumed $\theta \rightarrow \alpha$ transformation of aluminum oxide remains in the range close to the previous system – 1170 °C, slightly shifted to the left. According to [13], the presence of an exothermic peak at 1417 °C on the DTA-diagram characterizes the interaction of zirconium dioxide and carbon by reaction (5) (see fig. 3). Note, that some of the zirconium oxide has already interacted with aluminum.

Given that the amount of C in the initial mixture was calculated to interact with the entire volume of ZrO₂, a certain amount of carbon still remains in the mixture. The system also released the CO gas phase from the reaction (5). With the temperature increase C and CO interact with previously formed
intermetallide and the free zirconium, is also forming a carbide. In this case, the oxygen separated from the CO-gas interacts with the aluminum released from the intermetallide, forming Al₂O₃.

It can be assumed that the presence of some exo- and endoeffects at temperatures of 1510 °C and higher (see fig. 3) is associated with these chemical reactions. Compliance with their above assumptions in the framework of these studies has not been established.

Figure 3. DTA-thermogram, obtained by heating and cooling a sample from a mixture of ZrO₂(m)–21Al–7C % (wt %).

The roentgenogram taken from the sample of ZrO₂(m)–21Al–7C% (wt %) heated in a DTA analyzer contains peaks of two types: alumina and zirconium carbide (fig. 4). This indicates that the overwhelming amount of the intermediate phases formed in this system, including free zirconium, intermetallides, as well as the CO gas phase actively interact with the formation of stable compounds included in the final material.

Figure 4. X-ray diffraction pattern taken from a sample of ZrO₂(m)–21Al–7C (wt %) composition after heating in a DTA-analyzer
4. Conclusions

Studies based on the analysis of the interaction theory of reaction mixture components ZrO$_{2(m)}$–Al–C when heated to temperatures of 1650–1775°C, as well as experimental data of differential thermal and X-ray structural analyses of samples of stoichiometric compositions ZrO$_{2(m)}$–21Al–7C (wt %) and ZrO$_{2(m)}$–22Al (wt %), calculated from thermodynamically possible reactions of their interaction, allowed us to establish that:

1. The formation of Al$_2$O$_3$ and ZrC by heating the mixture ZrO$_{2(m)}$–Al–C system is a prerequisite for further study of the nature of structure formation in it, in order to synthesize dense functional oxide-carbide ceramic materials types, including instrumental purposes;

2. Formation Al$_2$O$_3$ in the system ZrO$_{2(m)}$–Al–C possibly as a result of direct interaction of Al with ZrO$_{2(m)}$, and by the decay of the intermetallide Al$_2$Zr, which is formed as an intermediate phase, subsequently interacting with the oxygen released from the previously formed gas phase CO; while ZrC is also synthesized, which formation is possible as the result of a interaction of zirconium oxide with carbon;

3. The formation of the final composition of components when heating a mixture of ZrO$_{2(m)}$–21Al–7C (wt %), is accompanied by a variety of exo- and endoeffects, which, in addition to the above interactions, are presumably associated with polymorphic transformations of aluminum oxide, as well as a some of chemical reactions caused by the formation of various compounds based on aluminum and zirconium.

5. References

[1] Merzhanov A G 1998 Combustion processes and material synthesis (Processy goreniya i sintez materialov) (Chernogolovka. ISMAN) p 512
[2] Gevorkyan E S 1989 Development of a composite material based on chromium oxide for a blade tool: avtoref. dis. Ph.D. (Kiev: Technical Sciences) p 26
[3] Prokopiv M N and Dzhelyalov S I 2005 Cutting ceramics. Status and development prospects Vestnik of SumGTU Sumy 11 (83) 129–34
[4] Chia T D, Vang T M, Zhao V and Liu T E 1999 Microstructure of Al$_2$O$_3$–TiC ceramics sintered by SHS-synthesis. J. Perspektivnye Materialy. 6 57–61
[5] Choi Yoon and Rhee Shi-Woo 1995 Reaction of TiO$_2$–Al–C in the combustion synthesis of Ti–Al$_2$O$_3$ composite. J. Amer. Ceram. Soc. 78 4 986–92
[6] Xia Tiandong Liu Tianzuo and Zhao Wenjun, Wang Tianmin 1997 The form of phases in the TiC–Al$_2$O$_3$ composites combustion synthesized from TiO$_2$–Al–C J. Gansu Univ. Tehnol. 1 16–20.
[7] Boudebane S, Boudebane A, Lembou S, Mechacht S, Benchiheb O and Boutefnouchet H 2002 The influence of additions on the self propagating high-temperature synthesis of TiC–Al$_2$O$_3$ ceramics. Annales de chimie. 27 (2) 1–15
[8] Thermodynamic Properties of Individual Substances. Fourth Edition 1990 Vol. 2 (Editors: Gurvich L V, Veyts I V, Alcock C B. Tab. Ed: Iorish V S). Elements C, Si, Ge, Sn, Pb, and Their Compounds. Hemisphere Publishing Corporation. Part One. Methods and Computation. XII+ 569 pp. Part Two. Tables. XII+372 pp
[9] Thermodynamic Properties of Individual Substances. Fourth Edition 1994 (Ed.: Gurvich L V, Veyts I V, Alcock C B. Tab. Ed.: Iorish V S, vol 3) Elements B, Al, Ga, In, Ti, Be, Mg, Ca, Sr, Ba, and Their Compounds. CRC Press and Begell House. Part One. Methods and Computation. VIII+707 pp. Part Two. Tables. XV+448 pp
[10] Chase M W, Davies C A, Downey J R, Frurip D J, McDonald R A and Syverud A N 1985 JANAF Thermochemical Tables. Third Edition. J. Phys. Chem. vol 14 1 1856
[11] Barin I, Knacke O and Kubaschewski O 1977 Thermochemical Properties of Inorganic Substances. (Berlin: Springer-Verlag) p 861
[12] Lyakishev N P, Bannіh O A and Rohlin L L oth. 1996 Binary state diagrams (Diagrammy sostoyaniya dvojnyh sistem) Directory In 3 v vol 1 (Moscow, Mashinostroenie) p 992
[13] Rogajlin, M I and Chalyh E F 1974 Carbon Graphite Handbook (Spravochnik po uglegraftitovym materialam) (Himiya) p 208
[14] Samsonov G V and Latysheva V P 1956 The study of the diffusion of boron and carbon in some metals of transition groups Physics of Metals and Metallography II (2) 309–11
[15] Samsonov G V and Epik A P 1962 To the question of the parameters of the reaction diffusion of boron and carbon into refractory transition metals Physics of Metals and Metallography vol XIV, 3 479–80
[16] Pavlinov L V and Bykov V N 1965 Carbon Diffusion in β-Zirconium (Physics of Metals and Metallography vol XIX) pp 397–400
[17] Kosolapova T Ya 1968 Carbides (Moscow, Metallurgiya) p 300
[18] Matrenin S V, Il'in A P, Tolbanova L O and Zolotareva E V 2010 Activation of sintering of oxide ceramics by additives of nanodispersed powders Bulletin of the Tomsk Polytechnic University 317 (3) 24–8
[19] Zharnylskaya A L and Volhin V V 2009 Synthesis of a ceramic precursor of the Al2O3 – ZrO2 system by the sol – gel method J. Vestnik Bashkirskogo universiteta (Bulletin of Bashkir University) 14 (3) 753–6
[20] Shishkovskij I V, Shcherbakov V I and Petrov A L 2001 Laser synthesis of refractory ceramics from Al and ZrO2 powders S.-T. J. Physics and Chemistry of materials treatment 3 45–8
[21] Natanzon Ya V and Petrishchev V Ya 1992 The interaction of zirconium with liquid aluminum saturated with zirconium. J. Poroshkovaya metallurgiya (Powder Metallurgy) 8 80–5