On the synthesis atmosphere influence in the technology of complex composite materials in the wide temperature range

A A Uspensky, S Yavshits, V Lipin, P Zhigalov, A Slobodov*
ITMO University, St.Petersburg, 197101, Russia
E-mail: aslobd@gmail.com

Abstract. Heterogeneous and homogeneous processes of synthesis for complex functional materials are studied by the methods of thermodynamic modeling and calculation, based on minimization of the Gibbs energy of the researched system. The conditions and products of gasification in the field of 0-2000 °C are determined for the synthesis conditions of a ceramic tile with complex composition (10-component system). All main products of interaction of components of ceramic mass (the system SiO$_2$ – K$_2$O – Na$_2$O – Al$_2$O$_3$ – Fe$_2$O$_3$ – CaO – MgO – TiO$_2$ – P$_2$O$_5$ – SO$_3$) and main components of air (the system N$_2$ – O$_2$ – CO$_2$ – H$_2$O) are found for the synthesis of material in the conditions of the air atmosphere at various temperatures. The character of physico-chemical influence of each components on the occurring processes is revealed, that determines a theoretical and calculation base of management and optimization of the synthesis engineering process for various functional materials.

1. Introduction
The synthesis atmosphere plays very important (and often decisive) role in the synthesis processes of modern functional materials. Its influence on phase and chemical materials transformations is most diverse under the synthesis of complex on composition (multicomponent, multiphase, etc.) - composites, ceramics and others.

These transformations and the systems are very complex - with multiple phases, many components, complexity and interconnection of the interactions and transitions, which take place during the synthesis, and wide range of values of state parameters, etc. Therefore, the detailed experimental research within the wide range of temperatures, compositions, and different conditions of synthesis is a very complex problem, which to date is generally unresolved [1-3].

In rather many cases it is correct and sufficiently effective to apply methods of the thermodynamic physico-chemical modelling. These methods have principal advantages in comparison to experimental methods, letting to obtain more detailed data about the whole complex of interrelated phase and chemical transformations corresponding to functional materials and products synthesis [4-8].

Therefore, revealing phase and chemical transitions, which occur when synthesising ceramics (and many other functional materials), phase and chemical composition of the pottery, and how technological and external conditions, i.e. temperature, pressure, synthesis atmosphere, humidity, influence these compositions, all have not only purely scientific interest, but and practical application as well [6, 7].

2. Methods and objects of the research
The main objects of investigation is the raw material for production of the complex functional
materials – ceramic tiles. As the basis of modelling, the raw material of a typical complex composition has been used (including all the main and auxiliary components). Its composition has been defined using analytical methods, and the main compounds have been recalculated into their oxide forms. As a result, oxide composition of the raw material corresponded to the ten-component system, which is the set of compounds-components fully and unambiguously describing both composition of the raw material, and the product. Then taking into account principal components of the synthesis atmosphere (air) the investigated multisystem can be represented as a set of the following 14 independent substances-components:

\[
\text{SiO}_2 - \text{K}_2\text{O} - \text{Na}_2\text{O} - \text{Al}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{CaO} - \text{MgO} - \\
- \text{TiO}_2 - \text{P}_2\text{O}_5 - \text{SO}_3 - \text{N}_2 - \text{O}_2 - \text{CO}_2 - \text{H}_2\text{O}
\]

The investigation has been undertaken with help of the methods and databases of thermodynamic modelling, which have been developed earlier, and which provide high correctness and efficiency of solution [4-8]. The equilibrium composition has been calculated under the different synthesis atmospheres and conditions, namely, in the temperature interval from low (room) temperatures to 2000°C (taking into account the possible overheating).

The considered conditions correspond to the annealing stage of the ceramic tiles production process. In the Table below, the initial data in mass and mole expressions are given for all 14 substances-components, taking into account losses during the annealing. Using mole composition is viable from the point of view of the of chemical and phase transitions analysis.

The first ten substances are the components of the synthesized material (its amounts are given in accordance with the composition of the ceramic mass), the last four ones - the main components of air (its amounts are given in accordance with the composition of humid air atmosphere).

**Table.** The chemical composition of the sintered ceramic material and the synthesis atmosphere (air)

| Substance | SiO₂ | K₂O | Na₂O | Al₂O₃ | Fe₂O₃ | CaO | MgO |
|-----------|------|-----|------|-------|-------|-----|-----|
| mas.%     | 55.20| 2.25| 0.45 | 13.68 | 3.19  | 9.72| 3.25|
| mol/kg    | 9.187| 0.239| 0.073| 1.342 | 0.199 | 1.733| 0.806|

| Substance | TiO₂ | P₂O₅ | SO₃ | N₂ | O₂ | CO₂ | H₂O |
|-----------|------|------|-----|----|----|-----|-----|
| mas.%     | 0.79 | 0.15 | 0.49| 73.99| 22.68| 0.00045| 1.244|
| mol/kg    | 0.099| 0.011| 0.117| 76.53| 20.53| 0.0003| 2.00 |

Let's consider synthesis in contact with the surrounding atmosphere. The composition of the atmosphere corresponds to the standard composition of the air into account of moisture (the Table). The pores volume has been taken as $10^{-4}$ m³/kg, which corresponds to the medium porosity of the pottery fragment.

It is possible to nominally separate three fields within the ceramic composition, in which the conditions of synthesis and nature of the phase and chemical interactions differ significantly. Therefore, the investigation has been taken for each of these fields:

1. Bulk of the ceramic phase, which is completely separated from the surrounding atmosphere, where no contact with the atmosphere, and formation and evaporation of the gases, being a
result of the transformations taking place, are impossible;
2. Domains in the ceramic mass, which do not contact with the atmosphere, but formation and evaporation of the gases are possible. Such conditions might take place on the boundary of the material and internal closed pores, which are not filled with the air;
3. Ceramic mass, which contacts with the air, i.e. surface of the material, or the boundary of opened or closed pores filled with the surrounding atmosphere.

Separate consideration of each from these cases allows to reveal the mechanism of each constituent of the complex physico-chemical transformations (in the bulk of the material, in gaseous phase, and on the phase boundary) and the contribution of each of them.

Of course, the main ones are the first type of these interactions - in the thickness of the ceramic mass (press-powder) between its components. They determine primarily the final phase and chemical composition of the synthesized material. However, we can’t ignore heterogeneous interactions of the second and the third types too - the formation of gaseous products and the influence of the synthesis atmosphere (inert gases, air, etc.).

Research as homogeneous and heterogeneous interactions is two difficult tasks, in many respects mutually independent and requires separate consideration. The main purpose of this paper is to study these heterogeneous interactions under synthesis of functional (ceramic) materials.

Next both types of the heterogeneous interactions are considered consistently. First, this type is an interaction between components of a ceramic mass with forming of gaseous products. Then - the same interactions, but with the participation of the synthesis atmosphere. Either inert gases or air (when it is admissible) are usually used as this atmosphere. The most complicated case, when air atmosphere is in contact with the ceramic composition, is considered here as a synthesis atmosphere. The most complicated case for synthesis atmosphere is considered here – when ceramic composition is in contact with air. The moisture content of the air has been taken into account too.

3. Results and discussion – gasification processes
Let's consider the case of phase and chemical transformations occurring in the bulk and pores of ceramic mass, when the surrounding atmosphere does not influence these transformations. This case is different from interactions only in bulk of the ceramic phase [7] by taking into account processes of the gaseous products yielded from reaction of the components of ceramic mass (but not only solid and liquid products).

Influence of temperature in the considered interval on the phase and chemical transformations obtained from the thermodynamic modelling of the considered system is presented in the Figure 1.

Analysis of the calculated data shows, that rising temperature form the room temperature to 1646 K, occurring in the reacting system (Figure 1) corresponds to the case of ceramic mass only for the corresponding temperature interval, when modelling has been performed for the conditions without the possibility to form gases [7]. Changes passing in the system are described by the corresponding reactions of complex oxides formation and decomposition most of all.

This shows that the processes of evaporation into vacuum become possible only at higher temperatures. Let's consider these processes.

At the temperature 1646 K calcium sulphate decomposes to yield sulphur(IV) oxide and oxygen. Release calcium oxide reacts with magnesium silicate MgSiO$_3$ and free silicon dioxide and forms calcium-magnesium silicate CaMg(SiO$_3$)$_2$ (dolomite):

$$2\text{CaSO}_4 + 2\text{MgSiO}_3 + 2\text{SiO}_2 \rightarrow 2\text{CaMg(SiO}_3)_2 + \text{O}_2 \uparrow + 2\text{SO}_2 \uparrow$$  \hspace{1cm} (1)
The following heating to 1725 K results in iron(III) oxide transforming to magnetite $\text{Fe}_3\text{O}_4$ with evolving oxygen:

$$6 \text{Fe}_2\text{O}_3 \rightarrow 4 \text{Fe}_3\text{O}_4 + \text{O}_2 \uparrow$$ (2)

It should be noted that the reaction of dolomite $\text{CaMg(SiO}_3)_2$ decomposition to silicates $\text{CaSiO}_3$ and $\text{MgSiO}_3$ under these conditions does not occur, since the calcium-magnesium silicate $\text{CaMg(SiO}_3)_2$ is stable in the absence of hematite $\text{Fe}_2\text{O}_3$.

Further temperature raise to 2000°C does not change chemical composition of the system.

4. Results and discussion - influence of synthesis atmosphere (air)

Now let's consider phase and chemical transitions in the ceramic mass when heated in the presence of air.
Influence of the temperature in the considered temperature range on the phase and chemical transformations, obtained as the result of thermodynamic modelling for the system under investigation, is illustrated by data in the Figure 2.

\[
\text{SiO}_2 \cdot \text{K}_2\text{O} \cdot \text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 \cdot \text{CaO} \cdot \text{MgO} \cdot \text{TiO}_2 \cdot \text{P}_2\text{O}_5 \cdot \text{SO}_3 \cdot \text{air}
\]
\[
V = 10^{-4} \text{ m}^3/\text{kg}
\]

\[n \text{ (mol/kg)}\]

\[\begin{array}{c}
\text{SiO}_2 \\
\text{CaAl}_2\text{Si}_2\text{O}_8 \\
\text{CaMg}(\text{SiO}_3)_2 \\
\text{KAISi}_3\text{O}_8 \\
\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} \\
\text{CaTiSiO}_5 \\
\text{Al}_2\text{TiO}_5 \\
\text{Fe}_2\text{O}_3 \\
\text{MgSiO}_3 \\
\text{NaAlSi}_3\text{O}_8 \\
\text{Fe}_2\text{O}_4 \\
\text{CatTiSiO}_4 \\
\text{CaSO}_4 \\
\text{O}_2 \\
\text{SO}_2 \\
\text{Ca}_4\text{P}_2\text{O}_9 \\
\text{Mg}(\text{PO}_3)_2 \\
\text{N}_2 \\
\text{NaNO}_3 \\
\text{KAI}_2(\text{SO}_4)_2(\text{OH})_3 \\
\text{CaCO}_3 \\
\text{CaCO}_3 \cdot \text{MgCO}_3 \\
\end{array}\]

\[T \text{ (K)}\]

\[300 \quad 600 \quad 900 \quad 1200 \quad 1500 \quad 1800 \quad 2100\]

**Figure 2.** Temperature influence on the phase transitions in the pores of pottery with air

At room temperature in the system the following compounds form: Al$_2$SiO$_5$, CaSO$_4$, Ca$_4$P$_2$O$_9$, CaCO$_3$, Ca$_3$Al$_2$Si$_3$O$_{12}$, CaTiSiO$_5$, CaMg(SiO$_3$)$_2$, Fe$_2$O$_3$, KAl$_2$(SO$_4$)$_2$(OH)$_3$, KAlSi$_3$O$_8$, NaNO$_3$, NaAlSi$_3$O$_8$, SiO$_2$, N$_2$.

From this it follows that interaction of the raw ceramic components is rather similar to the cases when synthesis atmosphere doesn’t influence on synthesis processes [********]. Besides this, the components of the air are considered as well. As the result of this, set of substances, which are absent in the system without air, is formed.

Oxygen, water vapours, and carbon dioxide are completely consumed when reacting with the ceramic mass.

Carbon dioxide reacts with calcium oxide to form calcium carbonate:
\[
\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3
\]  

(3)

Presence of water vapours in the gaseous phase results in formation of the compound \( \text{KAl}_2(\text{SO}_4)_2(\text{OH})_3 \), which fully consumes them by reaction with potassium, alumina, and sulphur oxides:

\[
\text{K}_2\text{O} + 2\text{Al}_2\text{O}_3 + 4\text{SO}_3 + 3\text{H}_2\text{O} \rightarrow 2\text{KAl}_2(\text{SO}_4)_2(\text{OH})_3
\]  

(4)

Part of the nitrogen reacts with sodium oxide and oxygen, yielding potassium nitrate:

\[
2\text{N}_2 + 2\text{Na}_2\text{O} + 5\text{O}_2 \rightarrow 4\text{NaNO}_3
\]  

(5)

This reaction goes to the complete consumption of the oxygen. Due to this, when equilibrium is reached, the gaseous phase becomes remaining nitrogen, which content in the air is approximately 77%.

In this way, one can see, that according to reactions (3)-(5), air actively reacts with initial oxides of the ceramic composition. As the result of this reaction gaseous system consists from nitrogen only at the room temperature. Let's consider the sequence of transformations, which occur in the system upon temperature raising.

At the temperature 307 K sodium nitrate becomes unstable and decomposes reacting with calcium alumosilicate, this results in formation of calcium nitrate and sodium alumosilicate \( \text{NaAlSi}_3\text{O}_8 \). This reaction also involves the aluminum silicate \( \text{Al}_2\text{SiO}_5 \) and silicon dioxide:

\[
2\text{Al}_2\text{SiO}_5 + \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 6\text{NaNO}_3 + 13\text{SiO}_2 \rightarrow 3\text{Ca(NO}_3)_2 + 6\text{NaAlSi}_3\text{O}_8
\]  

(6)

The further temperature rising to 372 K makes calcium nitrate unstable and breaks it into oxygen, nitrogen, and unstable calcium oxide. The latter reacts with aluminum silicate \( \text{Al}_2\text{SiO}_5 \) yielding calcium alumosilicate \( \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} \):

\[
\text{Al}_2\text{SiO}_5 + 3\text{Ca(NO}_3)_2 + 2\text{SiO}_2 \rightarrow \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} + 3\text{N}_2 + 7.5\text{O}_2
\]  

(7)

At the temperatures 392, 424, and 446 K the solid-phase transitions of various types occur for the corresponding temperatures.

Further temperature raising results in calcium carbonate becoming unstable at 451 K and reacting with alumosilicate \( \text{Al}_2\text{SiO}_5 \) and calcium-magnesium silicate \( \text{CaMg(SiO}_3)_2 \) to form dolomite \( \text{CaCO}_3 \cdot \text{MgCO}_3 \) and calcium alumosilicate \( \text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12} \):

\[
2\text{CaCO}_3 + 2\text{Al}_2\text{SiO}_5 + \text{CaMg(SiO}_3)_2 \rightarrow \text{CaCO}_3 \cdot \text{MgCO}_3 + 2\text{CaAl}_2\text{Si}_3\text{O}_8
\]  

(8)

At the temperature 456 K a series of interconnected phase and chemical exchange phase transformations occur (Figure 2).

At the temperature 480K dolomite becomes unstable and decomposes to carbon dioxide, and calcium and magnesium oxides, which react with silicon dioxide to form calcium-magnesium silicate \( \text{CaMg(SiO}_3)_2 \):

\[
\text{CaCO}_3 \cdot \text{MgCO}_3 + 2\text{SiO}_2 \rightarrow 2\text{CO}_2 \uparrow + \text{CaMg(SiO}_3)_2
\]  

(9)

Under temperature raising to the maximum calculated value of 2000 C all the interactions are the same to the ones above described for the corresponding temperatures when the absence of atmosphere, which shows that there is no interaction with the air of the ceramic material. In this case the gaseous phase has the composition corresponding to the composition of the air.

5. Conclusion

Models and quantitative data on heterogeneous interactions for conditions of synthesis of complex functional materials (10-15 components) are obtained by the methods of physico-chemical
thermodynamics.

Products and conditions of gasification are determined in a wide temperatures range of ceramic
materials synthesis.

The main solid-phase and gaseous products of interaction depending on temperature are determined
for the conditions of materials synthesis in the air atmosphere.

Influence of the main components of air (oxygen, nitrogen, carbon dioxide, moisture, etc.) on
course of phase and chemical transformations in sintered ceramic mass is revealed at temperatures
from 0 to 2000 °C.

The received results of modeling and calculations determine a basis for targeted management and
optimization of the synthesis engineering process of various functional materials.

References
[1] Saito H 1987 Reliability of technical ceramics and its recovery problems *Mater. Sci. Jap.* 34
N 12 26–31
[2] Gömze A L and Gömze L N 2013 Ceramic based lightweight composites with extreme
dynamic strength *Mater. Sci. Eng.* 47 012033
[3] Uspenskaya M V, Sirotinkin N V, Gorskii V A and Goloshchapov Yu G 2006 Composites of
acrylate copolymers and fullerene *Russ. J. Appl. Chem.* 79 858-860
[4] Yokokawa H, Fujishige M, Ujiie S and Dokiya M 1988 CTC: Chemical thermodynamic
computation system *J. Nat. Chem. Lab. Ind.* 83 N 11. 1–122
[5] Voronina T V and Slobodov A A 2011 Spectroscopic and thermodynamic study of heavy
water *Russ. J. Opt. Technol.* 78 N 3 156-160
[6] Olekhnovich R O, Volkova K V, Uspenskii A A, Slobodov A A and Uspenskaia M V 2015
Synthesis of poly(acrylic acid)-co-acrylamide/bentonite polymer nanocomposite as an absorbent
for removal of heavy metal ions from water *Proc. XV Intern. Multidisc. Sci. Geoconf.* 2 N 5
477-484
[7] Slobodov A, Uspenskiy Al, Yavshits S and Mischenko A 2015 Applicability of
thermodynamic modelling of phase-chemical composition and rheological properties for multi-
component natural and technological objects *Építőanyag – J. Silic. Based Compos. Mater.* 67,
164–167
[8] Uspenskiy Al, Slobodov A A, Gavrilov A, Radin M and Dahno V 2016 Nuclear power plants -
thermodynamic approach for ecological problems of radiation and water chemistry // *Proc. XVI
Intern. Multidisc. Sci. Geoconf.* 1 65-72