ON THE MECHANISMS OF SOLID-PHASE REVERSIBLE CHEMICAL REACTIONS IN THE MgO – Al₂O₃ – SiO₂ SYSTEM

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Results of an electron microscope study of metastable intermediate compounds formed due to the incompleteness of solid-phase processes in shaping materials of a corundum-mullite-cordierite phase composition are presented. The identification of high-temperature clinoclinorenic in contact with cordierite grains has made it possible to model and analyze some variants of mass transfer in the solid-phase reversible chemical reaction between mullite and spinel with the formation of corundum and cordierite. Common features in the mass transfer are determined for four reversible chemical reactions that occur in the subsolidus region of the MgO – Al₂O₃ – SiO₂ phase diagram under a normal pressure. This has made it possible to find and substantiate the most probable mechanisms of these reactions and the mechanisms of synthesis of triple oxide compounds, i.e., sapphirine and cordierite.

The phase diagram of the MgO – Al₂O₃ – SiO₂ system remains a subject of a permanent and never dying interest of ceramics specialists, because it is a physicochemical foundation of the majority of ceramic and refractory materials produced on a mass scale, and of geochemists, because it covers over 88% peridotites and other mantle rocks of the Earth. Despite the old and intent interest to the diagram it has not been studied sufficiently well. However, it can hardly be expected that new chemical compounds will be discovered in this system, and the development of new materials for different purposes should be based on nontraditional combinations of the known phases proceeding from the special features of the structure of the system. In the very important subsolidus region of the system such features are caused by the possibility of the occurrence of solid-phase reversible chemical reactions (SPRCR).

The first publication on an experimentally established SPRCR between sapphirine and corundum in the MgO – Al₂O₃ – SiO₂ system at 1460°C with the formation of spinel and mullite appeared in 1950 [1]. In this work the place of the field of primary crystallization of sapphirine in the diagram was analytically assumed to be small in size and lie far from the point of its composition. This crystallization field has not been localized experimentally until the present time and has been determined a priori from the results of a logical analysis. A formula of synthetic sapphirine, i.e., $M_4A_5S_2$, has been suggested in [1]. However, it has not yet been finally verified, which is admitted by the author. The same work presents a triangulation of the concentration triangle of the phase diagram with indicating that the $A - M_4A_5S_2$ conode is stable up to 1460°C. In many subsequent publications and copies of the diagram the respective dash line has been lost, and the possibility of the occurrence of this SPRCR in the high-alumina region has not been taken into account until recently. We have shown in [2] that today four SPRCR are considered possible in the subsolidus region of the MgO – Al₂O₃ – SiO₂ phase diagram under a normal pressure (the left-hand parts of the equations contain coexisting phases), namely,

\[
\begin{align*}
\text{Temperature, } & \text{°C} & \text{Reaction} \\
< 988 & 10MS + 2MA = 5M_2S + M_2A_2S_5 & (1) \\
988 - 1386 & 2M_2A_2S_5 + 15A = 4MA + 5A_3S_2 & (2) \\
1386 - 1460 & 4A_3S_2 + M_4A_5S_2 = 13A + 2M_2A_2S_3 & (3) \\
> 1460 & 4MA + A_3S_2 = 2A + M_4A_5S_2 & (4)
\end{align*}
\]

It should be noted that SPRCR can occur at a high pressure too, but with the participation of phases stable at the high pressure, specifically, pyrope garnet, and with the participation of what is known as aluminum enstatite, i.e., a solid solution of corundum in enstatite. The concentration of corundum $x$ in aluminum enstatite $MS \cdot xA$ can vary in a wide range, being more dependent on the temperature than on the pressure [3]. We know of high-baric SPRCR such as [3]

\[
\begin{align*}
M_3AS_3 + (1-x)M_2S = (4-x)MS \times xA + (1-x)MA, \quad (5) \\
xMA + (1+x)MS = MS \times xA + xM_2S, \quad (6) \\
xM_3AS_3 + 3(1-x)MS = 3MS \times xA. \quad (7)
\end{align*}
\]

A considerable experimental material has been accumulated on the order of the segregation of phases in the
Fig. 1. Appearance of the grain surface of cordierite inside a pore (a, ×45,000) and a characteristic surface border (b, ×54,000).

M – A – S system in heat treatment (for example, [4 – 6]). Such studies present a substantial interest for materials scientists but cannot be generalized due to the impossibility of constructing kinetic models for the process with the participation of the ternary compounds of the system for which the mechanism of the mass transfer in their formation has not been determined yet. We have shown in [2] that a SPRCR of the type (2') plays the most substantial role in the processes of phase formation in talc-kaolin-alumina compositions in the synthesis of cordierite-containing materials, and therefore we began the present study with it. We sought a single approach to the special feature of the mechanism of the realization of mass transfer in SPRCR (1) – (4).

Since we had to study the interphase processes in layers containing ultramicroamounts of polycrystals of intermediate phases with an expected size of 1 – 10 nm, we chose the method of electron microscopy, in particular, the method of microdiffraction from the singled-out region of the specimen.

The use of an accelerating voltage of 100 kV provided a resolution of 1 nm; the diffraction pattern was taken from the chosen region with a withdrawn diaphragm 1 μm in diameter. The specimen was a fine disperse powder sample marked by an index "0" as described in [2]. The powder sample was freely sprayed onto a copper supporting grid, and a single cordierite grain was chosen with the help of a NY-2E electron microscope. The directly studied region on the boundary of the grain was chosen under a 54,000-fold magnification provided by a transmission electron microscope EMV-100LM. The interplane distances were calculated from the positions of the diffraction rings and point reflexes in the electron dif-

fraction patterns. The preferable interactions between the cations in the reaction zone were compared by analogy with the estimation of the thermodynamic probability of conventional chemical reactions with the participation of the corresponding oxides under the assumption that the oxygen sublattice in the diffusion processes was inert.

The electron microscope study of the surface of cordierite grains exhibited regions with a well-manifested boundary on the contact between the phases and the cordierite grains, which had the form of semitransparent borders (Fig. 1a). It could be expected that the information on the structure of the material in the contact zones can throw light onto the mechanism of SPRCR (2'), the incompleteness of which due to the kinetic and steric deceleration is one of the causes of the formation of borders.