Synthesis and doping of fine-crystalline corundum in sub- and supercritical conditions

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Abstract. In the report the results of investigations of the mechanism and kinetics of the formation of cobalt doped corundum in water vapor medium are represented. Moreover, it is given the study result of changing of lattice position of cobalt ions and their state during synthesis. Aluminium hydroxide was using as raw material. Doping agent was cobalt nitrate. The doping of synthesis products (boehmite and corundum) occurs during their formation in solvothermal conditions and then in supercritical water fluid. The additives with reducing or oxidizing properties were brought in reaction medium. The products of the synthesis doped with cobalt were explored by various physicochemical methods: the X-ray phase-analysis, DR-spectroscopy, the magnetometry and SEM. It was found that the processes of the lattice rearrangement and doping take place simultaneously. In solvothermal conditions, below critical point cobalt ions are initially chaotically distributed in the interlaminar space of the boehmite structure. At supercritical conditions the doped boehmite transforms into cobalt doped corundum. Such crystals of corundum exhibit superparamagnetic properties. After heating in vacuum (1900°C) the corundum doped with higher concentrations of cobalt acquire the ferromagnetic properties. The authors guessed that cobalt ions aggregate into the nano-sized particles of cobalt in vacancies complexes of corundum structure.

Introduction

The transition to critical area (T>376°C, P>22 MPa) at hydrothermal synthesis allow producing pure materials with high performance and substantially shorten the duration of synthesis. Due to this the synthesis in supercritical fluids began to be widely utilized in an industry [1-4]. At comparison between mechanism of the hydrothermal process and process in SCWF becomes apparent that these mechanisms have certain common features [5, 6].

Previous investigations by authors of the mechanism and kinetics concerning the formation of fine-crystalline oxides in water vapor at both the sub- and supercritical conditions (P = 2–28 MPa, T = 200–450°C) and soft hydrothermal conditions have revealed that synthesis of fine crystalline oxides is a multistage process in these conditions. The process runs through formation of a solid-phase intermediate, which comprises the hydrated forms of the precursor [7, 8]. It was determined that molecules of fluid actively participate in the process of reorganization of the solid phase both during the first and second stages of transformation of precursors [9]. The processes of solid-phase transformations of oxides, oxyhydroxides and hydroxides during thermovapours treatment (TVT) proceed in conditions of dynamical quasi-equilibrium between solid phase and fluid. For example [10], the process of corundum formation from hydargillite in water passes through the following stages:

\[ \text{Al(OH)}_3 + \text{H}_2\text{O} \rightarrow \text{AlOOH} + \text{H}_2\text{O} \rightarrow a - \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O} \]

Hydargillite         Boehmite         Corundum
Conditions of the intermediate formation may affect the final stage of fine-crystalline oxides synthesis. The rate of the process and properties of the final product, such as a habitus, degree of perfection and sizes of crystals depends on of the specific structure of the intermediate [11].

The purpose of these investigations was to study the influence of cobalt ions on the synthesis process of corundum and its peculiarities, and to establish the mechanism by which the doping ions incorporate into the structure of the intermediate (boehmite) and synthesized corundum in a fluid water medium.

2. Materials and experimental methods

Synthesis and doping of solid oxides was carried out in laboratory (18 ml) and experimental-industrial (125 l) autoclaves. To synthesize doped boehmite and corundum, the hydrargillite of trademark "GD00" and, as dopant, Co(NO₃)₂·6H₂O were used. Because some substances were added in a reaction zone the redox potential of water fluid varied. Thus, H₂, H₂O₂, KOH, NH₃·H₂O were used. Necessary water vapor pressure was created in the autoclave by heated water, which was poured between the walls of the autoclave and the container with the raw material (hydrargillite). Hydrargillite including the dopant was initially held at a temperature in the subcritical range, then in the supercritical region.

The synthesized products were investigated by physical-chemical methods. The “Cam Scan Series 2” device was used to obtain SEM images of produced materials. X-ray analysis of the synthesized products was performed using X-ray powder diffractometer (STOE) with a CuKα and diffractometer DRON-3M. Diffuse reflection (DR) spectra were determined with a M-40 spectrometer.

3. Results and Discussion

X-ray diffractograms, DR spectra and performances of the curves of a magnetization of products arising from hydrargillite during synthesis of corundum doped by cobalt were analyzed, revealing the mechanism by which cobalt ions incorporated into the aluminous matrix. In water vapor, the transformation of hydrargillite into boehmite occurs very quickly at temperatures higher than 230°C. In figure 1, the kinetic curves of corundum formation from boehmite inclusive cobalt formed at 230°C are represented. The cobalt concentration relative to the produced corundum is equal to 0.1 mol of 1%. Molar relation of fluid and solid phase is 4.34. Coefficient of filling of free space of an autoclave is equal to 20%. Using this filling coefficient and at temperatures 400°C, 410°C, 420°C the pressure of water fluid is 26.8 MPa, 28.6 MPa and 30.4 MPa, respectively. The time of 100% formation of corundum from boehmite is 9, 4 and 3.5 hours, respectively. A long period of time is observed in the kinetic curve at 400°C, as the formation of boehmite up to the occurrence of the first crystals of corundum (induction period) (figure 1) requires the change in morphology and perfecting of the boehmite structure prior to the formation of corundum [12]. Boehmite has a layered structure (figure 2). The inclusion of dopant ions in the interlaminar space of boehmite structure occurs if it is
already in the subcritical range. The oriented growth of boehmite particles in blocks is also accompanied by capture of cobalt ions in macro-defects of the formative blocks (figure 3).

The absence of the expressed absorption bands in the visual field of the DR spectrum typical for cobalt ions regularly included in the crystal lattice denotes chaotic cobalt ions inclusion in the produced boehmite (figure 4a). As the endurance time of doped boehmite in water fluid medium increases, a wide absorption band appears at an interval 500 - 700 nm.

![Figure 4. DR spectra of the products TVT of hydargillite at T=400°C, P=26 MPa during: curve 1- 3 h, 2 – 12 h, 3 – 15 h, 4 – 22 h, 5 – 25 h, 6 -72 h.](image)

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The initial formation of corundum from doped boehmite is characterized by the resolution of this wide band to three bands at 550, 593 and 628 nm (figure 4d).

The ordering of boehmite and corundum structure with the increasing of duration of (TVT) is supported by the growth of the respective Bragg Scattering zones (figure 5).

The addition of fluid water (T = 410°C, P = 288 MPa) changes the redox potential of the substances and results in a change of a state of cobalt ions in doped corundum.

![Figure 5. Bragg Scattering zones of boehmite and corundum after TVT at T=400°C, P=26 MPa.](image)

Figure 5. Bragg Scattering zones of boehmite and corundum after TVT at T=400°C, P=26 MPa.

In the presence of hydrogen in fluid water the obtained corundum doped by cobalt is dark blue. The DR spectrum of this corundum (figure 6a) corresponds to a case of Co$^{2+}$ in tetrahedral coordination and the multiple transition $^4A_2(F) \rightarrow ^4T_1 (P)$ should be observed at nm 550 – 660 nm [13].

As the substances with oxidizing abilities are utilized, as the additives in a fluid, the synthesized corundum becomes green in color. The DR spectrum of this sample of corundum is characteristic for Co$^{3+}$ in octahedral coordination [13, 14]. The most intensive absorption bands in this case are positioned about 440 and 650 nm. The high-temperature heating of corundum doped with cobalt...
increases the absorption in all intervals in the DR spectrum (figure 7). The sample becomes dark grey or black depending on the content of cobalt. The absence of specific absorption bands has allowed us to make the inference that the cobalt ions, diffusing in a lattice of corundum crystal under heating, will agglomerate with formation nanoparticles of metallic cobalt. It is possible that formed nanoparticles are found in vacancy complexes. 

The comparison of figures 8 and 9 shows that heating the samples of corundum doped with cobalt at high temperature enhances their magnetic properties. After the heating at 1900°C (1 hour, in vacuum) magnetic moments ($\mu$) of samples become almost hundred times more (table). These samples have relatively high coercive forces (130 -230 Oe).

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|c|c|c|c|}
\hline
\textbf{Content % in medium Co} & \textbf{Saturation magnetization (G·cm$^3$/g)} & \textbf{Magnetic moment ($\mu$·10$^{-4}$)} & \textbf{Coercive force, (Hc Oe)} \\
\hline
& As-prepared & Heat-treated & As-prepared & Heat-treated & As-prepared & Heat-treated \\
\hline
1 & 1 & 0.003726 & 0.282885 & 2.4 & 200 & - & 130 \\
2 & 0.56 & 0.001269 & 0.234298 & 1 & 167 & - & 145 \\
3 & 0.26 & 0.003529 & 0.164688 & 2.1 & 111 & - & 230 \\
\hline
\end{tabular}
\caption{The magnetic performances of corundum doped by cobalt before and after heating at 1900°C}
\end{table}

The magnetic properties of the samples reduced during vacuum heating allow us to conclude that metallic cobalt particles are formed in oxygen vacancies due to elimination hydroxyls from corundum structure. The theoretical analysis of experimental hysteresis loops allowed the evaluation of the particle size distribution function for Co nanoparticles in the corundum lattice [15]. The size of Co nanoparticles averages 6 nm.

\textbf{Conclusion}

During the formation of corundum crystals from hydargillite in water vapor sequentially in sub- and supercritical conditions, the cobalt ions easily enter into the formed products structure. In subcritical conditions, the inclusion of a dopant happens chaotically in the intermediate [16]. Then, during formation of corundum, the cobalt ions are placed in tetrahedral or octahedral structural positions, exhibiting superparamagnetism. High-temperature annealing of doped corundum in a vacuum, with removal of residual hydroxyls from crystals structure and formation of vacancies complexes, results in the origin of nano-sized particles of cobalt placed in these defects.

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