THE PHASE TRANSFORMATIONS OF ALUMINA IN HYDROTHERMAL CONDITIONS

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The formation conditions of tohdite, $5Al_2O_3 \cdot H_2O$, under hydrothermal treatment of aluminium oxide or hydroxide are investigated. It is found that formation of tohdite and its morphology depend on a molar ratio a water fluid/Al_2O_3, the value of water fluid pressure, and presence of mineralizers.

INTRODUCTION

The phase transformations in system Al_2O_3-H_2O under hydrothermal conditions are caused by temperature limits of phases stability [1] (hydrargillite up to ~ 150ºC, boehmite and diaspore - up to 385ºC, corundum is higher 385ºC). In ours investigations [2-4] of transformation in hydrothermal conditions at 400ºC of aluminium oxide or hydroxide into boehmite and then into corundum it was not revealed of other intermediate products. However, in work [5] it is found that in hydrothermal conditions the formation of partially hydrated alumina - $5Al_2O_3 \cdot H_2O$ (tohdite) is possible. The tohdite was synthesized for the first time [5] as thin hexagonal plates at handling of boehmite or aluminum hydroxide at 450-500ºC in an autoclave filled on 80 % with a solution of mineralizer (aluminium fluoride or titanium (IV) sulfate). In the present work the conditions of tohdite formation are explored under hydrothermal treatment of aluminium oxide or hydroxide.

MATERIALS AND METHODS

In work was utilized aluminium hydroxide (hydrargillite of the mark GD00) and aluminium oxide obtained from the dehydration of hydrargillite at 400ºC in air. The raw material, aluminium oxide or hydrargillite was put in the container inside of autoclave (volume 16 cm^3). At treatment of aluminium oxide the water was filled in an autoclave outside of the container. The amount of water was complied with values of molar ratios of the water fluid/Al_2O_3 in a range 0.5-4. The samples 1 and 2 (table) were synthesized at the treatment of raw material in medium of water vapor. Hydrargillite is positioned in the container without adding water in an autoclave. The amount of hydrargillite is taken so that the evolved structural water has created the prescribed pressure (1.5-3.0 МПа). The filled autoclave is positioned in the hot furnace with temperature 400-422ºC. The autoclave heated up up to temperature of furnace during 1-1.5 hours. The duration of isothermal heating varied from 1 till 300 hours. The sample 3 (table) was synthesized from hydrargillite in the presence of aqueous solution of manganese chloride. Content of Mn^{2+} ions has made in reaction medium 0.5% in calculation on Al_2O_3. The autoclave heated up stepwise at first at 270ºC, and then at 410ºC (on a second stage of heating the pressure has made 29 MPa). The transformation products were explored by X-ray methods (diffractometer Stoe), by IR-spectroscopy (EQUINOX 55/S in a region of 4000-400 cm^{-1}) and by morphological analysis (electron microscope “Cam Scan Series 2”). The thermal analysis and thermogravimetric measurement were performed using thermoanalyser SDT Q600 (TA). Diffuse reflection (DR) spectra were measured using spectrometer Specord M40 in range of 220-800 nm ($BaSO_4$ check standard).

RESULTS AND DISCUSSION

The hydrothermal treatment of aluminium oxide or hydroxide at 400°C with molar ratio the water fluid/Al_2O_3 more than 1.5 leads to formation at first of a boehmite and then corundum [2-4]. At diminution of a molar ratio a water fluid/Al_2O_3 the process of formation of a boehmite and corundum from hydrargillite is decelerated (**Figure 1**), and at values of a molar ratio less than 1.5 in

transformation products a partially hydrated alumina - tohdite ($5Al_2O_3 \cdot H_2O$) appears. At values of a molar ratio 1-0.7 a process proceeds only on a path of formation tohdite (**Figure 2**, *1*). And even increasing of a molar ratio (and pressure of water fluid up to 30 MPa) the formed tohdite phase is conserved, not transforming into corundum.

Table

Sample	Starting material	Reaction medium and (water fluid/Al_2O_3) molar ratio	TºC	Time of treatment	Content of water, %
1	Al_2O_3	Water fluid, (1)	400	3 day	3.6
2	$Al(OH)_3$	Water fluid, (3)	410	4 day	3.73
3	$Al(OH)_3$	Water fluid, (1.2); content of Mn^{2+} ions in reaction medium is 0.5%	270 410	3 day 7 day	-

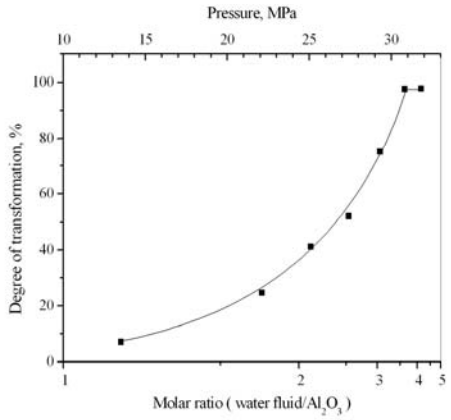
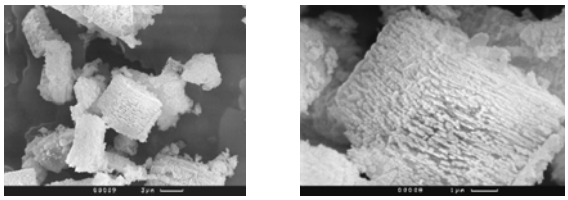


Figure 1. Dependence of transformation degree of boehmite into corundum on a molar ratio a water fluid/Al_2O_3 during 1.5 hours at 422°C.



a *b*

Figure 3. Morphology of tohdite particles: *a* - general shape of particles, *b* - shape of plate-like crystals.

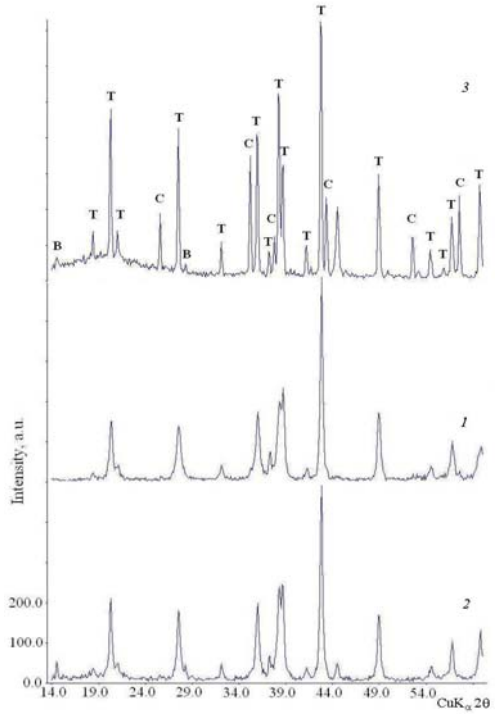
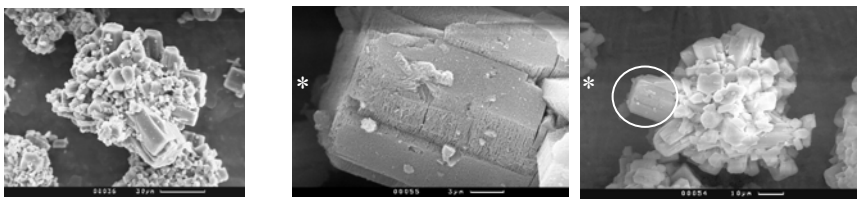


Figure 2. X-Ray diffraction pattern of samples synthesised from Al_2O_3 (*1*) and $Al(OH)_3$ (*2*, *3*).
T – tohdite, C – corundum, B – bohemite.



a *b*

Figure 4. Starting particles of gibbsite (*a*), tohdite (*b*) synthesized from hydrargillite at 410°C and pressure of water vapor 3 MPa (sample 2).

The morphology of tohdite obtained under treatment of aluminium oxide at 400ºC with molar ratio the water fluid/Al_2O_3 = 1 is shown in **Figure 3**. It is visible that the particles consist of small plates. The particles of tohdite (sample 2, **Table**) formed at treatment of hydroxide in medium with low pressure of water vapour (3 MPa, **Figure 4**, *b*) have the similar shape. It is visible that the formed tohdite retains the shape of starting particles of gibbsite

(**Figure 4**, *a* and *b*).

The synthesized sample 2 contains tracks of boehmite (**Figure 2**, 2). The content of structural water is 3.73 % (**Figure 5**). It exceeds theoretical value 3.41 % calculated for $5Al_2O_3 \cdot H_2O$ due to an impurity of boehmite. The dehydration of boehmite proceeds at 533°C. The dehydration of tohdite happens at higher temperature 706°C.

The unit cell dimensions calculated from the X-ray data are *a*=5.57372, and *c*=8.76534 Å. These values agree well with cell dimensions of tohdite synthesized under hydrothermal treatment of $\eta-Al_2O_3$ at 460°C and 30 MPa [6].

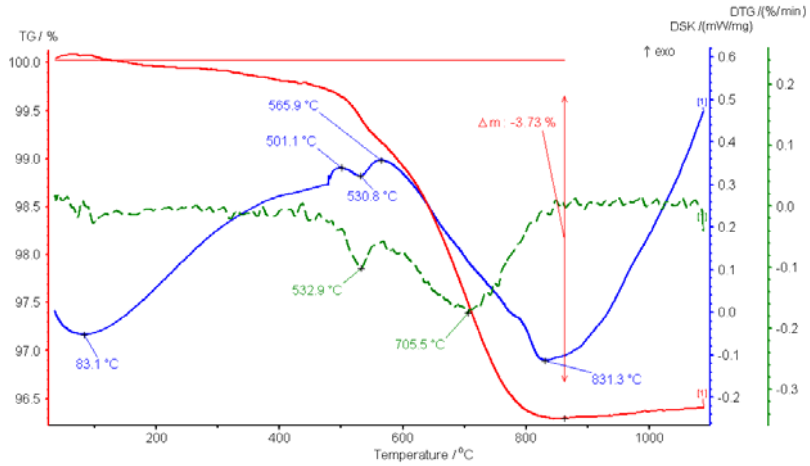


Figure 5. Thermogravimetric measurements of sample 2.

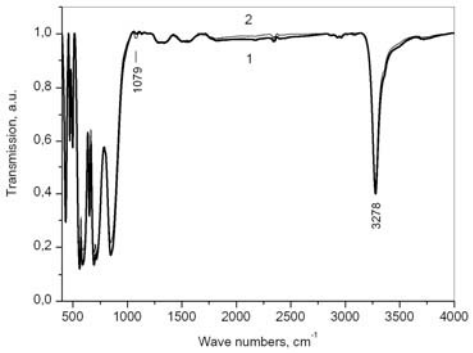


Figure 6. Infrared spectra of tohdite samples synthesized from Al_2O_3 (1) and aluminium hydroxide (2).

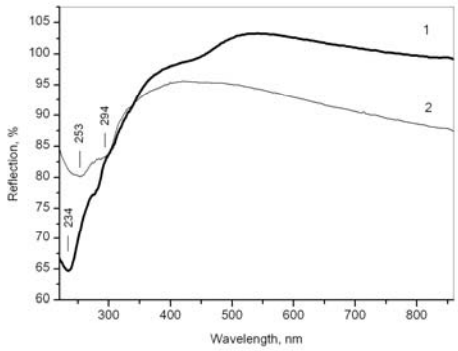


Figure 7. The diffuse reflection spectra of tohdite samples synthesized from Al_2O_3 (1) and aluminium hydroxide (2).

The presence in IR-spectrum (**Figure 6**) of narrow band at 3278 cm^{-1} testifies to homogeneity of hydroxyl groups on bond energy. The presence in structure of oxygen vacancies is other characteristic feature of oxides formed in medium of water fluid. They are manifested in UV region of DR spectrum (**Figure 7**) as absorption bands of F-centres, which are defects [7] on the basis of oxygen vacancies.

The tohdite of sample 3 synthesized in the presence of Mn^{2+} ions and at the greater pressure of water vapours, than in a case of samples 1 and 2, has the well formed thin plate-like crystals (**Figure 8**). The impurity of corundum is simultaneously formed also (**Figure 2**, *3*). The crystals of corundum have the greater size and isomeric habitus (**Figure 8**). The synthesis of tohdite in the form of well formed thin plate-like crystals was observed also under hydrothermal conditions with increased pressure of water fluid of 30-100 MPa [5, 6].

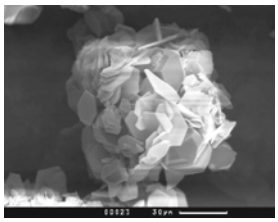


Figure 8. Thin plate is tohdite, large crystals is corundum.

The solid phase transformation of oxides with formation of well formed face of crystals at a heating in medium of water vapour happens relatively easily. In our opinion [8-10] it results from increased defect formation and occurrence of structural mobility due to processes of reversible hydroxylation. In acts of hydroxylation - dehydroxylation occur the processes of formation and breakage of bonds Me-O-Me. They are accompanied by formation of oxygen vacancies and residual hydroxyl groups. The decrease of water vapour pressure leads to diminution of intensity of processes of reversible hydroxylation, diminution of the content of hydroxyl groups in alumina structure and diminution of structural mobility. It leads to formation of tohdite phase ($5Al_2O_3 \cdot H_2O$) instead of boehmite ($Al_2O_3 \cdot H_2O$), influences the habitus perfection of crystals. The depressing of solid-phase mobility appears in formation of poorly formed plate-like crystals of tohdite (**Figure 3, 4**). From this standpoint the role of mineralizers (ions Ti, F, Mn) consists in participation in a defect formation and diminution of the content of hydroxyl groups in alumina structure during transformation. The presence of mineralizers brakes transformation. For magnification of mobility of structure the increase of temperature (up to 480-500°C) and pressure (up to 80-100 MPa) is necessary [6].

CONCLUSION

The decrease under hydrothermal treatment of oxide or hydroxide of aluminium of a molar ratio (water fluid / oxide) up to values less than 1.5, and the depressing of pressure, or the adding into reaction medium of mineralizers (ions Ti, F, Mn) results in diminution of alumina structure hydroxylation with formation of tohdite. Under treatment of formed tohdite in water medium with increased pressure and 400°C the solid-phase transformation into corundum does not happen.

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