THE INFLUENCE OF FLUID COMPOSITION ON THE FORMATION MECHANISM AND PROPERTIES OF CORUNDUM AND QUARTZ SYNTHESIZED IN SUPERCRITICAL CONDITIONS.

Danchevskaya M.N.*, Torbin S.N., Ivakin Yu.D., Ovchinnikova O.G., Muravieva G.P.
Chemistry Department, Moscow State University, Moscow 119992, Leninskie Gory Russia
E-mail: mardan@kge.msu.ru Fax: 7 095 939 32 83

The influence of additions of different substances in supercritical water fluid on mechanism and kinetics of process of solid-phase transformation silica and alumina and on the properties formed crystals was investigated. The process of solid-phase transformation was realised in autoclave at 400°C and water vapour pressure 20.0 – 26.0 MPa.

The investigations have shown that depending on composition of fluid the process of transformation of precursor proceed on various mechanisms and with formation of corundum and quartz various habitus and crystals size.

INTRODUCTION

The solid-phase processes of formation crystals quartz and corundum in supercritical water fluid (SCWF) are utterly susceptible to additions of some substances. At that a mechanism and kinetics of solid-phase transformation of precursor in supercritical water change [1, 2, 3].

MATERIALS AND METHODS

The processes of formation of quartz crystals from amorphous silicon dioxide (silica) and corundum crystals from aluminum hydroxide (hydrargillite) in water fluid using different additions of volatile substances were studied. As additions were used $(CH_3)_4NOH$; $NH_2CH_2CH_2OH$; N_2H_5OH; NH_4OH; C_2H_5OH; ? ? $_3$? ? ; $(NH_2)_2CO$. Another the process of corundum synthesis in supercritical alcohols was investigated.

The interaction of the additions in supercritical water with silicon dioxide was investigation by mass spectrometry and EPR. The EPR signals were registered for irradiated silica by rays Co60 at –196°C. The process of solid-phase transformation was realised in autoclave at 400°C and water vapour pressure 20.0 – 26.0 MPa. For investigation the products of transformation SiO_2 on varies stages was used the methods of X-ray analysis.

RESULTS AND DISCUSSION

The investigations have shown that the process of transformation of amorphous silicon dioxide in a crystalline state proceed on various mechanisms and with formation of various intermediate crystalline phases depending on composition of additions in water fluid.

The mass spectrometric and electron paramagnetic resonance study have shown, that under supercritical water fluid the added volatile substances interact with surface hydroxyls of silica with formation amino- or methoxy- and ethoxy-groups. In the case the using the additives containing $C_mH_{2m+1}O$- groups, promote the formation of quartz through an

intermediate state primarily of keatite. The habitus of these quartz crystals are needle – prismatic primarily (Figure 1). The nitrogen – containing additives direct to the structurization of silica through intermediate crystalline phase - cristobalite. In this case final crystals of quartz had isometric bipyramidal habitus (Figure 2).

The influence of the various composition additives in water fluid is exhibited not only in modification structure of intermediate phase during crystallisation of silicon dioxide, but also in increase of phase changes rate and rate of crystalline structure perfection of modifications of silicon dioxide.

As the perfection criterion of crystalline phase was size of the Bragg Scattering Zone (D), which was defined on a broadening X-ray reflexes, {101} - for cristobalite {201} - for keatite and {101} - for quartz.

In Figure 3 the values D of cristobalite, obtaining from amorphous silicon dioxide in supercritical water with differing additives, are given. In Figures 4 and 5 the similar dependences for keatite and quartz are presented.

In a general view, the dependence D = f (t) is featured by the equation $D^n_i - D^n_o = k\tau$, where τ - time of water vapour treatment of silicon dioxide. The constant n depends on the mechanism of formation of mosaic structure blocks of crystals [4, 5]. From Figure 3 it is shows that the values D of cristobalite, irrespective of composition of the additives, will increase linearly with time of water vapour treatment. At the same time, D_o strongly depends on composition of the additives. D_o reflect features of the mechanism of generation of a new phase nucleuses. The linear form of the equation (1), n = 1, corresponds to process of the silica globules coalescence with formation floccules with structure of cristobalite (Figure 6).

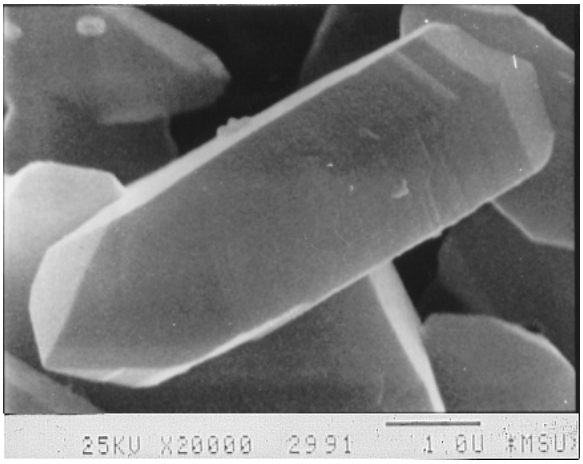

Figure 1. The quartz formed through intermediate crystalline phase – keatite.

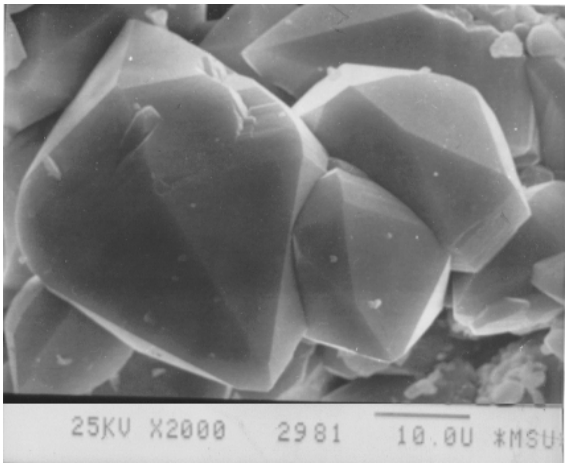

Figure 2. The quartz formed through intermediate crystalline phase – crystobalite.

In a case keatite n = 5, process of new phase formation, controlled by diffusion of substance on boundaries of globules, result in accretion of globules on phase boundaries. In this case arises fibrous phase (Figure 7), which transforms in keatite.

The process of structure perfection of quartz, formed both from keatite, and from cristobalite, is circumscribed by the equation (1) with n = 3. It corresponds to process elimination of pores in quartz crystals.

By this means, the characteristics of final product of crystallisation (fine-crystalline quartz) such as habitus and size of crystals and degree of perfection of crystals depend on composition of the additives in a water fluid.

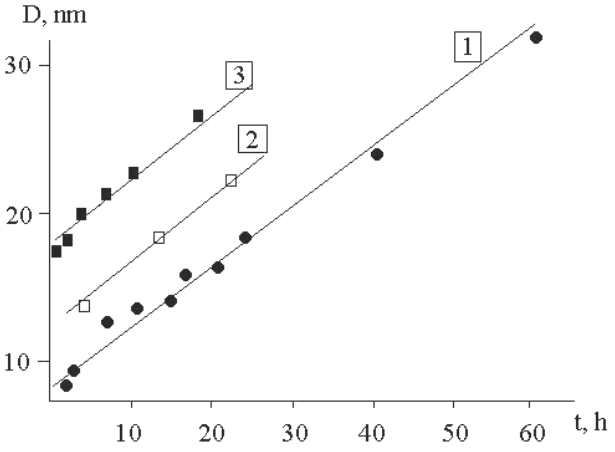

Figure 3. The increase of the size of the Bragg scattering zone (D) versus time (t) of treatment of cristobalite in SCWF.
1 – tetramethylammonium hydroxide,
2 - methanol, 3- ethanol.

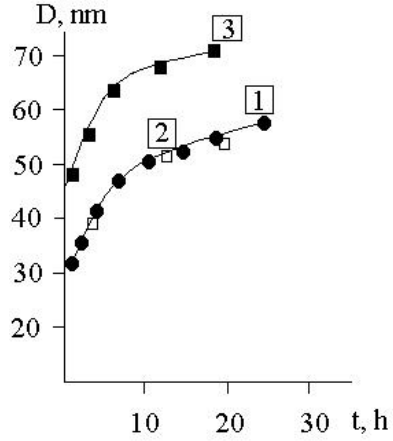

Figure 4. The increase of the size of the Bragg scattering zone (D) versus time (t) of treatment of keatite in SCWF.
1 – tetramethylammonium hydroxide,
2 - methanol, 3- ethanol.

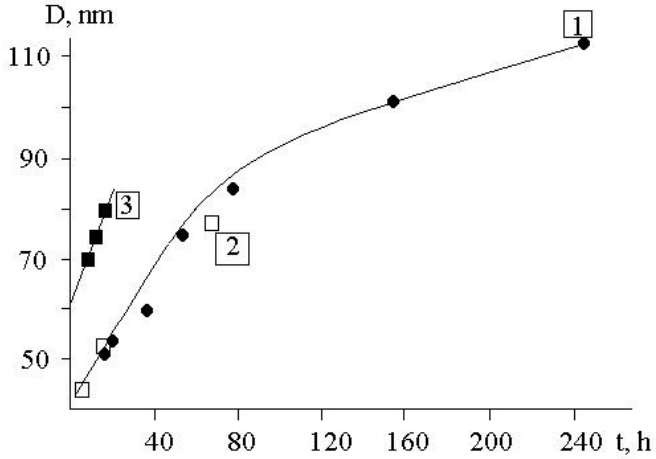

Figure 5. The increase of the size of the Bragg scattering zone (D) versus time (t) of treatment of quartz in SCWF: 1 – tetramethylammonium hydroxide, 2 – methanol, 3 – ethanol.

The influence of composition of a fluid on solid-phase transformation of aluminum hydroxide is exhibited already at the first stages of this process. It was shown earlier [1] in atmosphere super critical water hydrargillite transforms in corundum through intermediate substance – boehmite: $Al(OH)_3$? AlOOH + H_2O ? a-Al_2O_3.The rate of formation, habitus and size of corundum crystals depend on temperature, pressure and composition of a fluid.

Figure 6. The intermediate fibrous phase silica predecessor of keatite.

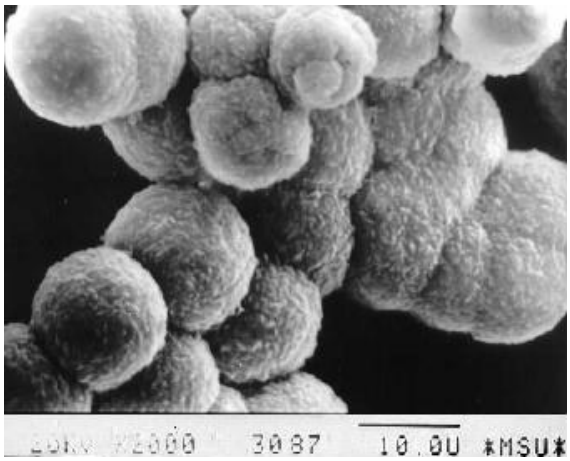

Figure 7. The floccules with structure of cristobalite.

The usage of the additives of volatile substances in SCWF has allowed governing the size and habitus of synthesized crystals of corundum. So the additives in SCWF of the boron – contained substance (for example, H_3BO_3) in amount up to 0.1 mol % result in formation of corundum crystals in the shape of hexagonal prisms with the size 20 - 30 microns (Figure 8). In this case the rate of formation corundum decreases. Whereas the nitrogen – containing substances (NH_4OH; $(CH_3)_4NOH$; N_2H_5OH; $(NH_2)_2CO$) added in SCWF accelerate of formation corundum, increase the size of crystals and generate crystals isometric bipyramidal habitus (Figure 9).

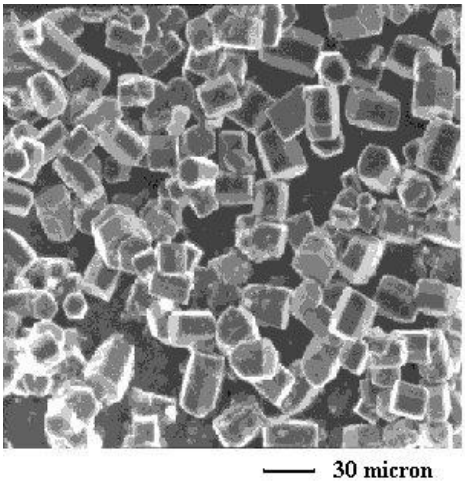

Figure 8. Corundum, synthesized in SCWF with the additive H_3BO_3.

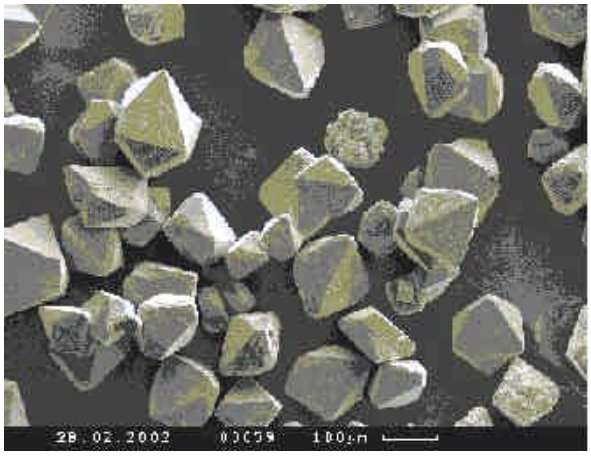

Figure 9. Corundum, synthesized in SCWF with the additive NH_4OH.

The influence of fluid composition on process of crystals formation of corundum is exhibited already at a stage of formation of intermediate substance - boehmite. During synthesis of corundum in SCWF and in SCWF with nitrogen-containing substances boehmite is generated in the shape distorted parallelepipeds (Figure 10).

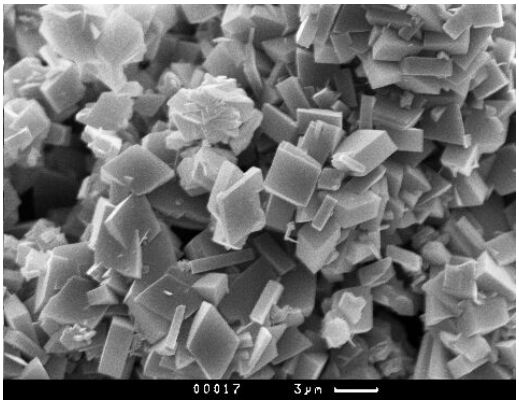

Figure 10. The boehmite obtained in SCWF with additive NH_4OH.

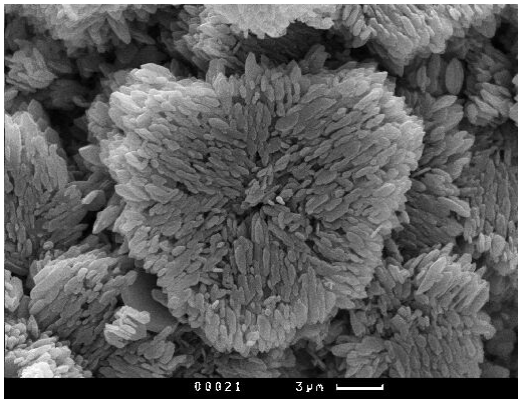

Figure 11. The boehmite obtained in methanol.

If during synthesis of corundum the fluid of primary alcohols will be utilized instead of water fluid the habitus of corundum and boehmite will be varied.

The primary alcohols are be pyrolyzed and the products of catalytic pyrolysis of boehmite interact with structural hydroxyls, producing groups ($C_mH_{2m+1}O$-Al-) on a surface and in volume of boehmite. It changes habitus of generated boehmite, keeping standard crystallographic form.

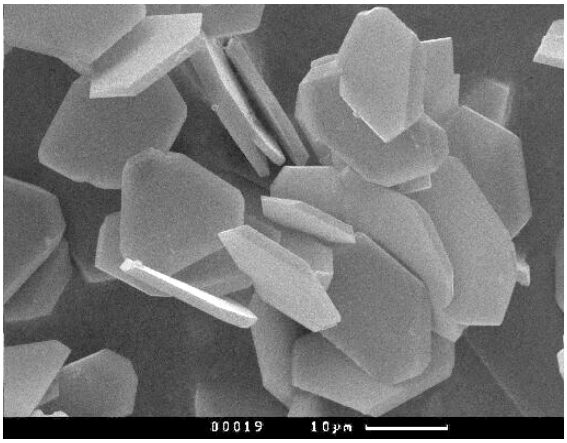

Figure 12. The corundum obtained in methanol from boehmite (T = 400°C; P = 15 MPa).

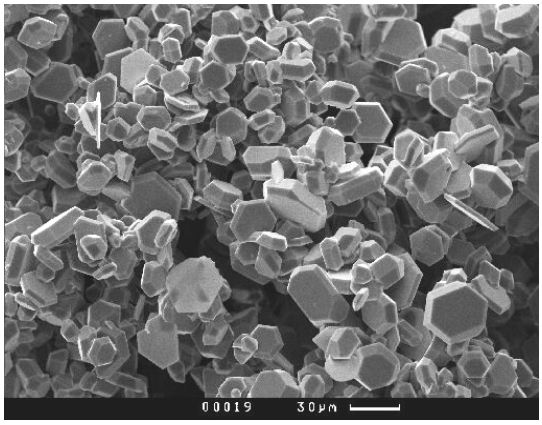

Figure 13. The corundum obtained in methanol from hydrargillite (T = 400°C; P = 15 MPa).

In Figure 13 the corundum synthesized from hydrargillite in fluid of methanol is shown. It represents incrassate hexagonal plates. If raw material is boehmite, synthesized from hydrargillite in water fluid, and then heat treated in a fluid of methanol or ethanol, also the corundum plates will form (Figure 12).

Changing a relation the water / alcohol during synthesis of corundum it is possible to obtain the corundum different habitus: from thin plates up to hexagonal prisms and bipyramids.

In Figure 14 is shown, as the width of corundum plates decreases depending on the content of methanol in fluid methanol/ water. At definition of composition of fluid it was

taken into account water, which is coming out structure of hydrargillite or boehmite at synthesis of corundum.

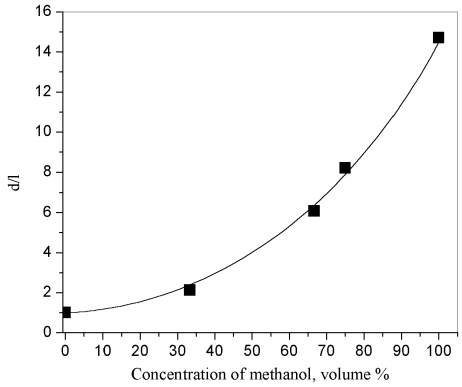

Figure 14. The dependence of the relation of diameter (d) of plate crystals of corundum to thickness (l) versus the content of methanol in SCWF.

CONCLUSION

The results of the investigations have shown high sensitivity of solid-phase processes to composition of a fluid. Introduction in reaction system of the additives capable to interact with hydroxyl groups of intermediate substance, boehmite at synthesis of corundum, or hydroxylated cristobalite and keatite at synthesis of quartz, results in formation of crystals certain habitus and size. In case of the additives nitrogen - containing substances the crystals rhombohedral habitus will be generated, at usage of the additives containing alkyl-group - hexagonal prisms of different thickness. At complete replacement of an water fluid by fluid of primary alcohols, for example by methanol or ethanol, the process of solid-phase transformation of hydrargillite in corundum in supercritical conditions flows past on the similar mechanism (with formation of intermediate substance - boehmite), with close time of transformation, but with changed habitus both boehmite, and corundum.

It is possible to assume that the water, which is coming out structures of a hydrargillite or a boehmite, ensures normal realization of process. Really, at usage as raw material anhydrous oxide aluminum in supercritical alcohol fluid corundum will not arise. There is ordering only the structure of oxide aluminum.

REFERENCES:

[1] DANCHEVSKAYA, M. N., TORBIN, S. N., MURAVIEVA, G. P., OVCHINNIKOVA, O. G., IVAKIN, YU. D., Reactivity of Solids, Vol. 5, **1988**, p. 293.
[2] DANCHEVSKAYA, M. N., IVAKIN, YU. D., TORBIN, S. N., PANASYUK, G. P., BELAN, V. N., VOROSHILOV, I. L., High Pressure Research, Vol. 20, **2001,** p. 229
[3] DANCHEVSKAYA, M. N., OVCHINNIKOVA, O. G., Russian Journal of Physical Chemistry, Vol. 62 (1), **1988**, p. 64.
[4] GOBLE, R.L, J. Appl. Phys., Vol. 32, 5, **1961**, p. 780.
[5] NICHOLS, F.A., J. Appl. Phys., Vol. 37, 12, **1966**, p. 4599.