

ROLE OF WATER FLUID IN THE FORMATION OF SOLID PHASE OXIDES

Yu. D. Ivakin *, M.N. Danchevskaya, S.N. Torbin, V.A. Kreisberg, L.F. Martynova
E-mail: Ivakin@kge.msu.ru fax: (095) 932-8846
Chemistry Department of Moscow State University, 119899, Moscow, Russia

The role of an aqueous medium in solid-phase processes of structure transformation of hydroxides and oxides of metals is shown. The restructuring of oxides proceeds due to processes of hydroxylation - dehydroxylation of oxides structure in conditions of quasiequilibrium with a water vapour.

INTRODUCTION

The technology of fine-crystalline materials based on processes of solid-phase transformation of structure of hydroxides and metal oxides in water vapour at the temperature range of 250-400°C and pressures 10 - 30 MPa is circumscribed [1,2]. The carrying out of transformation in a water vapour leads to the acceleration of a process or to realization of it in soft conditions. For example, a growth of corundum crystals (α -Al₂O₃) in hydrothermal conditions is carried out at temperatures of 450-600°C and pressures about 100 MPa [3], while in a water vapour the formation of well edged fine-crystalline corundum from gibbsite or aluminum oxide happens for 7-20 hours at 350-400°C and pressures less than 30 MPa [4]. In the same conditions the amorphous silicon dioxide is transformed into well edged fine-crystalline quartz (α -SiO₂) [5]. The hydrothermal synthesis Y₂Mn₂O₇ goes on in a solution of NaClO₃ and NaOH at 500°C and pressure 300 MPa within 10 hours [6]. However, the synthesis of Y₂Mn₂O₇ in a water vapour is finished for two hours at 400°C and a pressure of 26 MPa [7].

The study of kinetics of solid oxides transformation under thermovapour conditions showed, that the processes are going by the solid-phase mechanism and are accompanied by the change the of structural water content [1]. The transformation proceeds through the intermediate hydroxylated phase formation [1,2,5]. The present report is devoted to the study of a role of an aqueous medium in solid-phase processes of transformation of hydroxides and oxides of metals at temperatures of 150-400°C and pressures of 1 - 26 MPa.

MATERIALS AND METHODS

Precursor - gibbsite {Al (OH)₃} was obtained by Bayer method; aluminum oxide was obtained by calcinating of gibbsite. Another aluminum oxide was obtained by calcinating of pseudoboehmite, which was synthesized by hydrolysis of secondary aluminum butoxide. The yttrium oxide and amorphous silicon dioxide were of the mark «special purity».

The thermovapourous treatment (TVT) of raw material have been carried out in laboratory (volume 17 cm³) autoclaves. For the creation of a water vapour pressure in the autoclave, the water filling of a free volume was no more than 20%. The TVT have been carried out at temperatures of 150-400°C and pressure of water vapour of 1-26 MPa. The raw material placed into the container made from a stainless steel or teflon with the cover, which was installed into autoclave on the support. The water solution was introduced into autoclave outside of the

container. Autoclave was heated in an isothermal condition during certain time, then was cooled. Autoclave was rapidly cooled due to steeping of the autoclave bottom in water. Thus inside autoclave the water was condensed at the bottom below than container with a sample, which remained dry. The dry product was discharged from the autoclave and was investigated by physicochemical methods. The X-ray analysis of the products was carried out at various stages of oxides transformation using a diffractometer DRON-3M. The perfection criterion of a structure of obtained crystalline product was a size of Bragg scattering zone (D). The determination of a water content and identification of different water forms have been studied by means of mass-spectrometry (MI-1311), thermal analysis (Derivatograph Q-1500 D) and IR - spectroscopy (Specord IR-75). The IR-spectroscopy, photoluminescent spectroscopy of intrinsic and impurity defects, X-ray analysis and definition of parameters of unit cells were utilized for the observation of the structural transformations and the defect formations. The photoluminescence was registered by SDL-2M spectrometer in a range of 200-1200 nm.

CONCLUSION

The transformations of oxides in a water vapour start from the hydroxylation of their structure. In a case of TVT of amorphous silicon dioxide at 400°C the water content in SiO₂ structure increases in 4 times (fig. 1) and achieves 2,2-3%. The specific surface and density decrease, and the structure remains amorphous [2]. Then at occurrence of intermediate crystalline phases - cristobalite and keatite the water content in a structure of TVT products starts to decrease. The drop of water content is continuing then during the formation of a terminating phase - quartz (α -SiO₂). The appearing crystalline phases have at first the disordered structure, but then in conditions of TVT the dehydroxylation of solid phases and perfecting of their crystalline structure happens (fig. 1, line 4, 5): the sizes of Bragg scattering zone grow. The perfecting of structure of a quartz is prolonged also after the final transformation [8]. The ordering of quartz structure is accompanied also by diminution of the content of structural water. The water content decreases from 1000 up to 300 ppm as a result of an increase of a TVT duration of obtained fine-crystalline quartz till 100 hours. It is important to mark, that the structuring of hydroxylated silicon dioxide which happens in the conditions of TVT is accompanied not only by diminution of water content in it, but also by the change of a state of hydroxyl groups in the matrix of silicon dioxide. The increase of a temperature of maximal rate of the water removing (fig. 2) from structure of products together with the increase of TVT time of silicon dioxide also testifies to it.

The interaction of aluminum oxide with liquid water or with the water vapour leads to the formation of various products. The transformation of aluminum oxide in a atmosphere of water vapour depends on the temperature of the process, pressure of water vapour and initial state of oxide. γ -Al₂O₃ is transformed to boehmite, and then into corundum at 400°C and the filling of autoclave on 20%. At a decrease of autoclave filling up to 2-3 % tohdite (5Al₂O₃·H₂O) will be obtained, which even at the raise of filling of autoclave by water up to 20 % is not transformed into corundum. It is necessary to point out, that under hydrothermal conditions tohdite was obtained [9] from boehmite or gibbsite at 450-500°C and the autoclave filling of 80 % at the presence of fluoride of aluminium. θ -Al₂O₃ is transformed to boehmite (γ -AlOOH), and then to diaspore (β -AlOOH) under the atmosphere of water vapour at temperatures of 200-300°C. The dependence of diaspore generation rate from the conditions of θ -Al₂O₃ treatment was measured

after the content of diaspore in its intermixture with boehmite in the samples synthesized within 14 hours. In the presence of water vapour the rate of a process has a maximum at 270°C with a formation of 37% of diaspore. In liquid water under the same conditions less than 2 % diaspore (fig. 3) will be obtained. At temperatures of γ -Al₂O₃ treatment higher than 300°C the corundum is a final product. The transformation of gibbsite into boehmite also proceeds with different rates in a liquid water and in a water vapour. So, gibbsite does not vary under heating in the air at 180°C within 10 hours. However, the treatment at 180°C in autoclave under water vapour leads to the complete transformation of gibbsite into boehmite during 3 hours. If the gibbsite treatment at 180°C is performing in water, the rate of transformation to boehmite is decreased two times. The similar effect was mentioned in [10]. The transformation gibbsite into boehmite is ended in 0,5 hours with the increase of treatment temperature in water vapour in autoclave up to 200°C. Under the atmosphere of water vapour gibbsite is transformed into boehmite and then into corundum [1, 2, 4] at temperatures of 380-420°C and pressures of 10-30 MPa. The transformation of boehmite to corundum is accompanied by long induction period of 6-30 hours depending on impurities in gibbsite. The change of water content in boehmite was studied by the quasiisothermic thermogravimetric method. Thus it is revealed, that in boehmite, synthesized at 200°C within 86 hours, the water content in a structure is of 16,1% at a stoichiometric water content of 15,01%. The hydroxyl groups in a structure of this boehmite consist of two types which distinguish in a character of removal during the heating in the thermogravimetric analysis. The part of hydroxyl groups - about 1 % - (feebly coupled) is removed out at temperatures of 320-450°C and thus the structure of boehmite is maintained. The other 15,1% part of hydroxyl groups (strongly connected) is removed at temperatures of 450-490°C with destruction of the boehmite structure and the formation of γ -Al₂O₃. With the increase of TVT temperature of boehmite synthesis the total water content and the relation of types of hydroxyl groups in structure boehmite depend on the TVT duration (fig. 4). During the TVT of boehmite at 400°C the relation of two types of hydroxyl groups varies. After one hour of TVT the feebly coupled groups does not remain in a structure of boehmite. Such boehmite contains less structure water (14,4 %) accordingly to stoichiometric of composition. At the end of an induction period the water content decreases to 14,3 %. Dehydroxylation of boehmite is accompanied by the increase of the size of Bragg scattering zone (from 36 to 63 nm), which happens during an induction period and after it while boehmite is present at system. The boehmite structure perfecting is also indicated by a drop in a luminescent emission, which corresponds to diminution the defect content in the boehmite structure. The prolongation of boehmite dehydroxylation after terminating an of an induction period leads to the formation of thermodynamically stable phase of α -Al₂O₃. The formed corundum has at first disordered structure, which is promptly perfected [4]. However the corundum structure modification continues yet during a long time TVT (fig. 5). In the corundum crystals the decrease of hydroxyl groups also are maintained. Under corundum heating in vacuum they go out from the structure at temperatures of about 400°C (338 ppm) and more 1000°C (173 ppm). Thus, at structuring in TVT conditions of both aluminum oxide, and silicon dioxide, there is a change of the content and state of hydroxyl groups in a matrix of oxide.

The similar processes proceed at solid-phase formation of oxide composite from the mixture of simple oxides. For example, the synthesis of yttrium-aluminum garnet (YAG, Y₃Al₅O₁₂) proceeds in a medium of water vapour of and in liquid water under treatment of stoichiometric of oxides mixture of yttrium and aluminium in the temperature range of 260-400°C

and water vapour pressures of 4.8-26 MPa. The YAG formation is preceded by the induction period of 1 h at 300°C and 6 h at 270°C. During induction period the hydroxylation of starting oxides happens with the formation of crystalline hydroxide of yttrium and amorphous feeble hydroxylated aluminium oxide. The shaping of YAG starts with the decrease of the content of hydroxyl groups (fig. 6, a) and the change of their state in a structure of products (fig. 6, б). During the process the intermediate rehydroxylation of transformation products is observed. Thus, the change of the content of hydroxyl groups is determined by the change of their state in a matrix of oxides. In the formed YAG the residual hydroxyl groups are maintained. The content of hydroxyl groups decreases with increase of time of treatment in a water vapour (fig. 6, a) and with growth of temperature. At synthesis temperature increase from 300°C up to 400°C the water content in a final product decreases from 8,35 % up to 5,44%.

The obtained results allow to conclude, that in the beginning of oxides interaction with water vapour the hydroxylation of structure predominates. With the increase of the hydroxyl groups content in a structure the rate of dehydroxylation becomes comparable with a rate of hydroxylation, approximating a state of a product to quasiequilibrium with the water vapour. Breakage and the originating of bonds Me–O–Me and Me–OH in the acts of hydroxylation - dehydroxylation define the increase of defects content [8] and solid-phase mobility of a matrix of oxides. The restructuring of structure of oxides in the conditions of quasiequilibrium with an aqueous medium proceeds due to takeoff and accumulation in defect structure of local sites (clusters) with a major lifetime. The structure of clusters includes hydroxyl groups, ions of oxide - "master" and "visitor". In simple oxides the role of "visitor" is fulfilled by microadditives of activators of transformation, and in binary systems - ions of the second oxide. During a process of clusters dehydroxylation the nucleuses of a new phase with defect structure will be formed. Then the nucleuses grow, and their structure is perfected. Obviously, the difference of rate of structure transformation in conditions of hydrothermal and thermovapour treatment is stipulated by features of dissociative adsorption and absorption of water by oxides during the contact with vapour and condensed phase.

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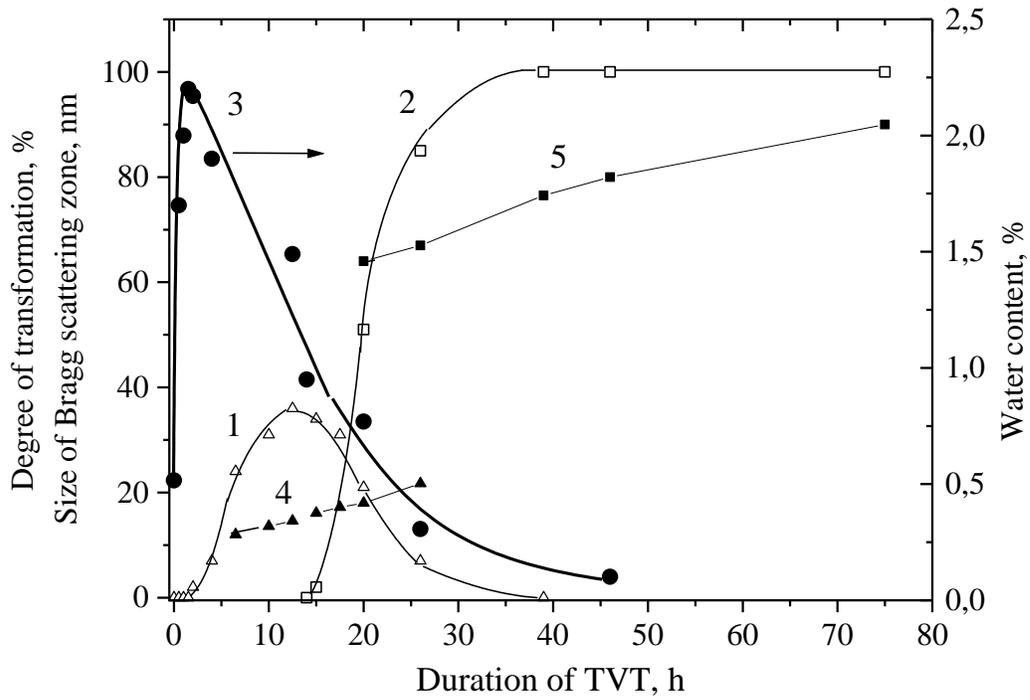


Fig. 1.

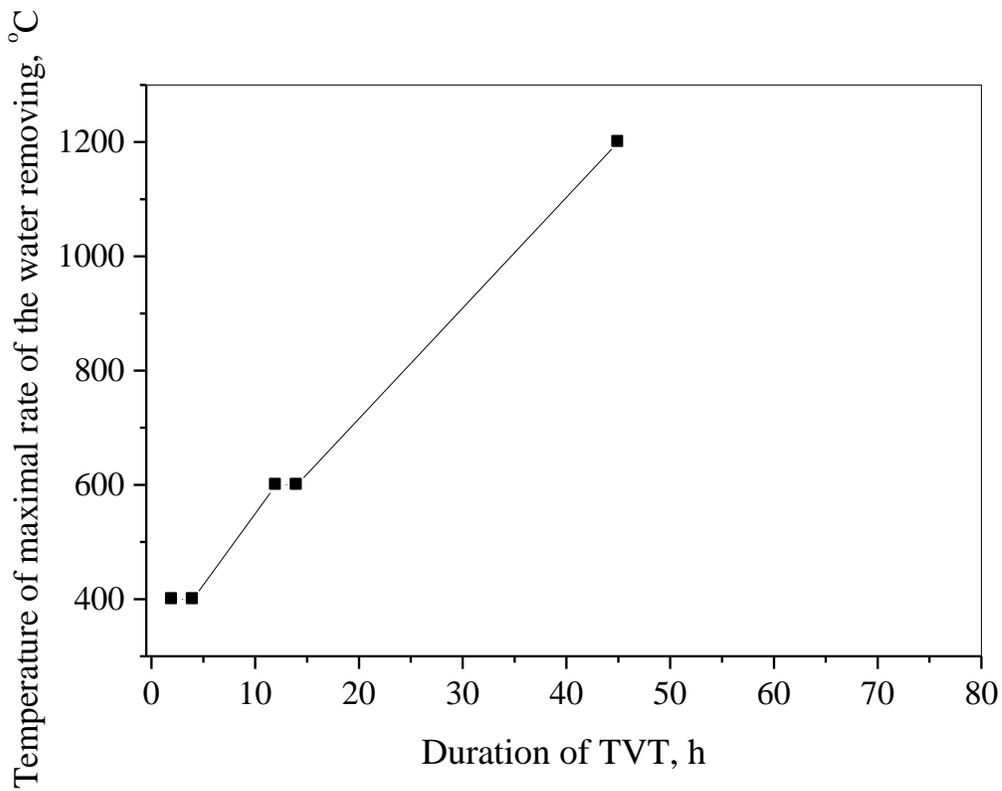


Fig. 2.

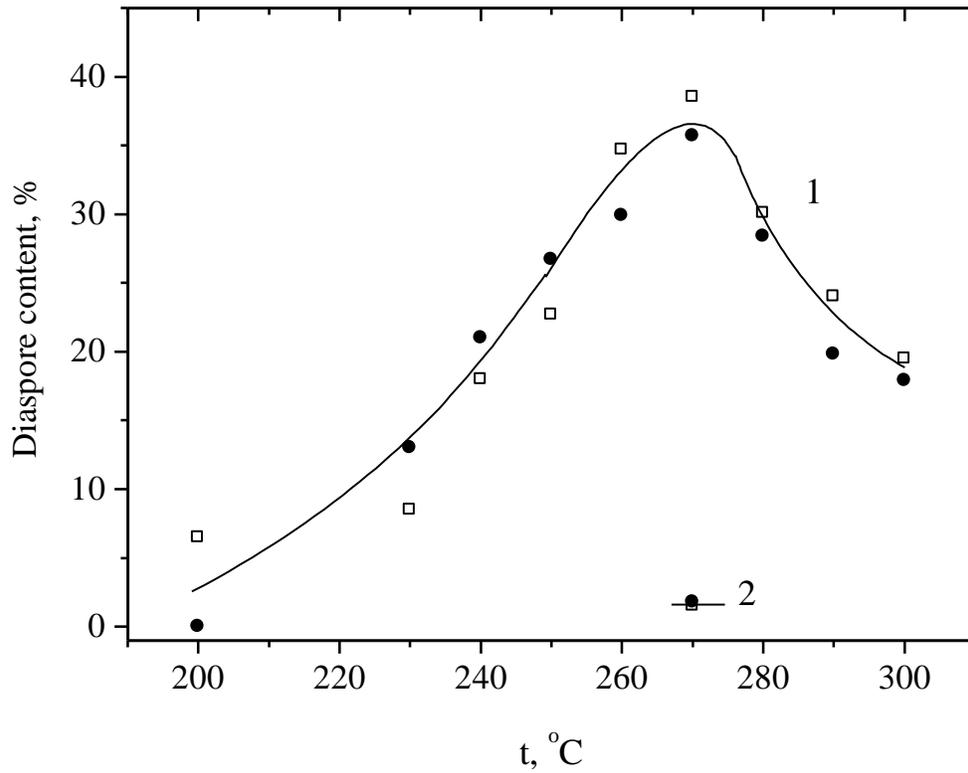


Fig. 3.

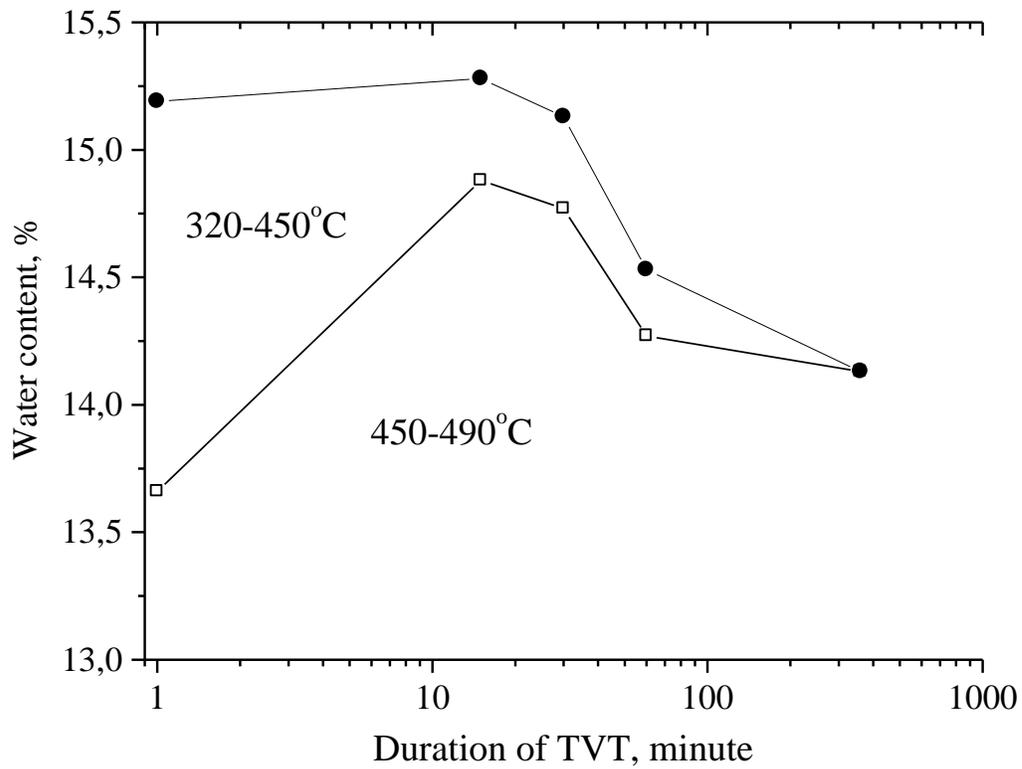


Fig. 4.

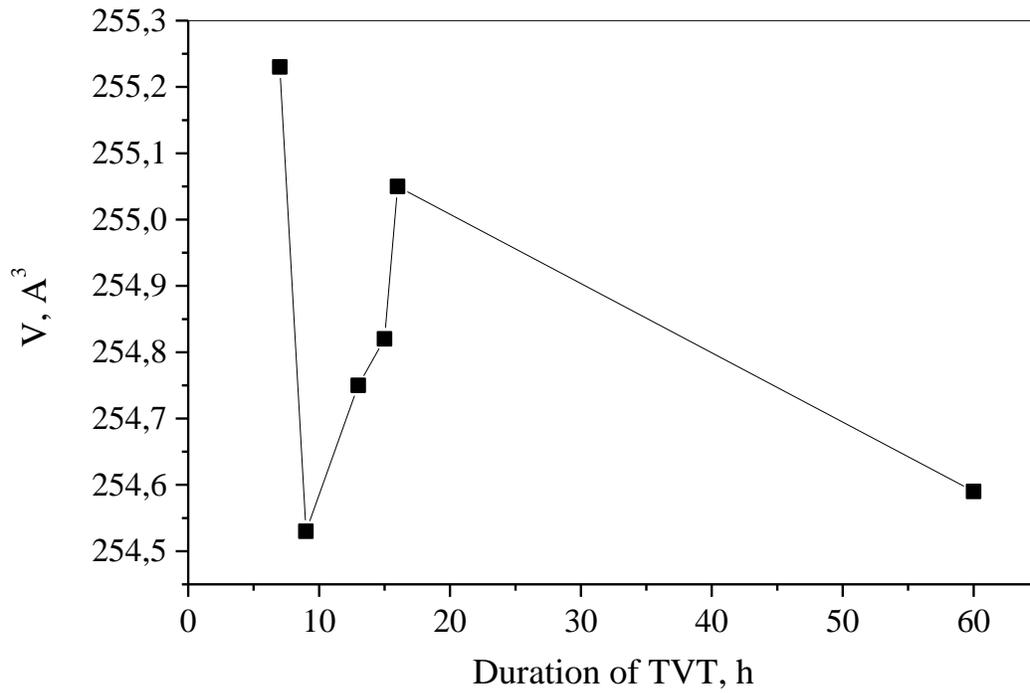


Fig. 5.

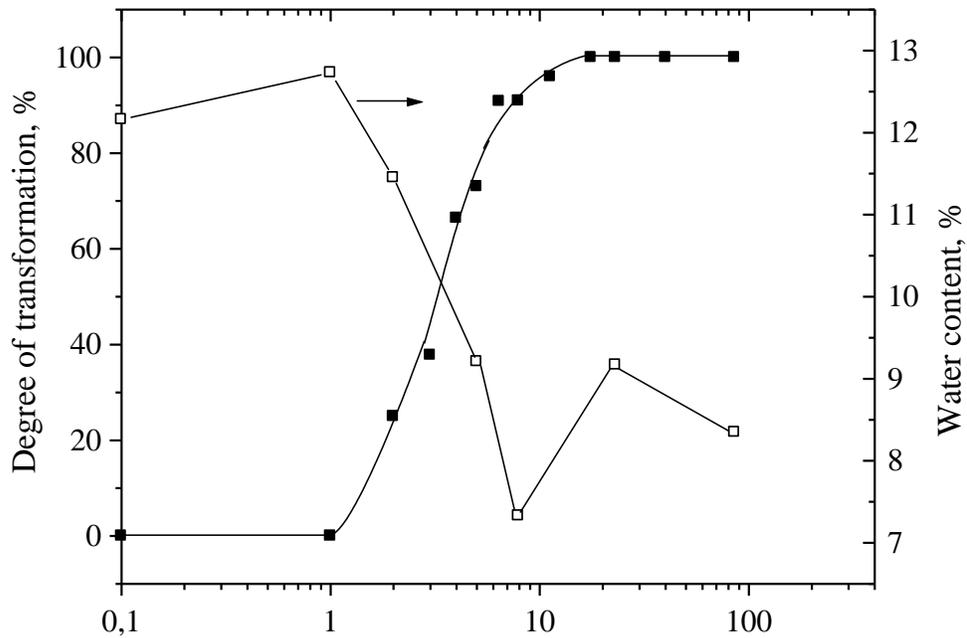


Fig. 6. a

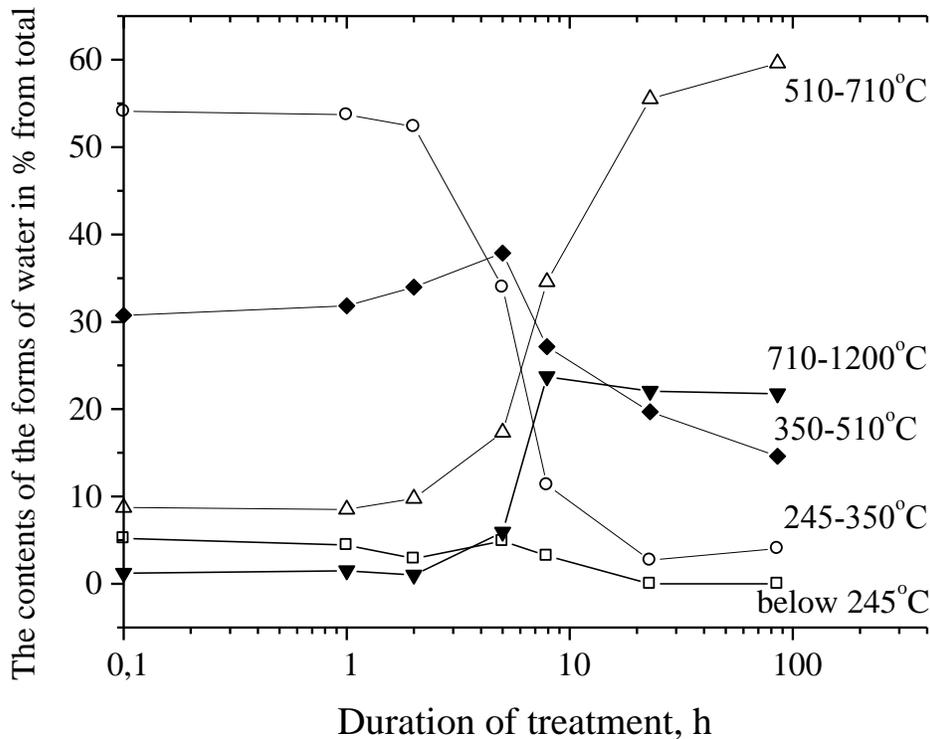


Fig. 6. b

Figures captions:

Figure 1. Transformation of amorphous silicon dioxide under TVT at 400°C and pressure water vapour of water 24 MPa: change of the content cristobalite (1), quartz (3) and water (3) in products of transformation, and also dimensional change of the size of Bragg scattering zone cristobalite (5) and quartz (6).

Figure 2. Dependence of temperature of maximal rate of water removal in vacuum (at mass - spectrometer measuring) on the TVT time of silicon dioxide.

Figure 3. The diaspore content in a mixture with boehmite in samples obtained by TVT of θ - Al_2O_3 at various temperatures within 14 hours: 1 - treatment in a water vapour, 2 - treatment in water.

Figure 4. Change of water content in structure of boehmite during the TVT at 400°C. The temperatures of removal of two types of hydroxyls are indicated.

Figure 5. Change of unit cell volume of structure of corundum during TVT.

Figure 6. a - Change of degree of transformation (1) and water content (2) in structure of products during of treatment of an mixture of aluminum and yttrium oxides at 300°C in water; **b -** change of relative content of the water oozed in indicated temperature ranges at a heating on air of products of synthesis YAG at 300°C.