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(54) **PROCESS FOR PRODUCING
NANOCRYSTALLINE ALPHA- Al_2O_3**

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(57) **ABSTRACT**

A process is claimed for producing nanocrystalline $\alpha\text{-Al}_2\text{O}_3$ that is characterized in that nuclei are added to aluminum chlorohydrate, which is subjected to thermal treatment within less than 30 minutes, the resultant agglomerates being comminuted.

PROCESS FOR PRODUCING NANOCRYSTALLINE ALPHA- Al_2O_3

[0001] The present invention relates to a process for producing nanocrystalline α - Al_2O_3 , also referred to as corundum, very finely disperse crystallization nuclei, preferably α - Al_2O_3 nuclei, first being added to aluminum chlorohydrate in the form of a solution as starting material, which is then subjected to a thermal or thermophysical reaction.

[0002] Ultrafine alumina powders are used in particular for ceramic applications, for matrix reinforcement of organic or metallic layers, as fillers, as polishing powders, for the production of abrasives, as additives in paints and laminates and for further special applications. The production of the ultrafine alumina powders is effected either by chemical synthesis, mechanical comminution methods or a thermophysical route.

[0003] The chemical synthesis generally involves precipitation reactions (hydroxide precipitation, hydrolysis of organometallic compounds) with subsequent calcination. Frequently, crystallization nuclei are added in order to reduce the transformation temperature to α -alumina. The sols thus obtained are dried by an inconvenient procedure and thus converted into a gel. The further calcination then takes place at temperatures of from 350° C. to 650° C. For the transformation to α - Al_2O_3 , ignition must then be effected at temperatures of about 1000° C. The processes are described in detail in DE 199 22 492.

[0004] A further route for obtaining nanomaterials is the aerosol process. There, the desired molecules are obtained from chemical reactions of a precursor gas or by rapid cooling of a supersaturated gas. The formation of the particles is effected either by collision or the constant vaporization and condensation of molecular clusters in equilibrium. The newly formed particles grow through further collision with product molecules (condensation) and/or particles (coagulation). However, if the coagulation rate is greater than that of new formation or of growth, agglomerates of spherical primary particles form.

[0005] Flame reactors represent a production variant based on this principle. Here, nanoparticles are formed by the decomposition of precursor molecules in the flame at 1500° C.-2500° C. The oxidations of TiCl_4 , SiCl_4 and $\text{Si}_2\text{O}(\text{CH}_3)_6$ in methane/ O_2 flames may be mentioned as examples and lead to TiO_2 and SiO_2 particles. With the use of AlCl_3 , it has been possible to date to produce only the corresponding alumina. Flame reactors are used today industrially for the synthesis of submicroparticles, such as carbon black, pigment TiO_2 , silica and alumina. It has not been possible to date to produce nanoscale corundum in this way.

[0006] Small particles can also be formed with the aid of centrifugal force, compressed air, sound, ultrasound and further methods, also from drops. The drops are then converted into powder by direct pyrolysis or by in situ reactions with other gases. Spray-drying and freeze-drying may be mentioned as known processes. In spray pyrolysis, precursor drops are transported through a high temperature field (flame, oven), which leads to rapid vaporization of the readily volatile component or initiates the decomposition reaction to give the desired product. The desired particles are collected in filters. The preparation of BaTiO_3 from an aqueous solution of barium acetate and titanium lactate may be mentioned as an example here.

[0007] By milling, it is also possible to attempt to comminute corundum and to produce crystallites in the nano range thereby. The best milling results can be achieved with stirred ball mills in wet milling. Milling beads comprising a material which has a greater hardness than corundum must be used. However, this method is characterized by high wear of milling beads, contamination of the product with the material of the milling beads, an enormous time requirement and a very high energy consumption.

[0008] A further route for the production of corundum at low temperature is the transformation of aluminum chlorohydrate. Nuclei, preferably comprising very fine corundum or hematite, are likewise added thereto for this purpose. For avoiding crystal growth, the samples must be calcined at temperatures of about 700° C. to not more than 900° C. The duration of the calcination here is at least 4 hours. A disadvantage of this method is therefore the great time requirement and the residual amounts of chlorine in the alumina. The method was described in detail in report DKG 74 (1997) No. 11/12, pages 719-722.

[0009] The disadvantages of the processes according to the known prior art are that the yields per unit time are low owing to the long calcination times or, in the case of milling, the product is contaminated and is still too coarse.

[0010] The object of the present invention is therefore to produce nanocrystalline corundum by a process which gives high yields in a short time with minimum energy supply. The product produced should be redispersible by simple means and hence capable of giving stable nanosuspensions.

[0011] Contrary to the statements by various authors to date (report DKG 74 (1997) No. 11/12; DE 199 22 492), this object can be achieved starting from aluminum chlorohydrate (aluminum hydroxychloride).

[0012] Surprisingly, it was found that nanocrystalline corundum can be produced within a few minutes on calcination of aluminum chlorohydrate.

[0013] The invention relates to a process for producing nanocrystalline α - Al_2O_3 , nuclei being added to aluminum chlorohydrate and the latter being subjected to thermal treatment, and the agglomerates thus obtained being comminuted. The duration of the thermal treatment is less than 30 minutes.

[0014] The starting point for the process according to the invention is aluminum chlorohydrate, which is attributed the formula $\text{Al}_2(\text{OH})_x\text{Cl}_y$, where x is a number from 2.5 to 5.5 and y a number from 3.5 to 0.5 and the sum of x and y is always 6. This aluminum chlorohydrate is mixed as aqueous solution with crystallization nuclei, then dried and then subjected to a thermal treatment (calcination).

[0015] 50% strength aqueous solutions of aluminum chlorohydrate, as are commercially available, are preferably used as starting material. Crystallization nuclei which promote the formation of the α -modification of Al_2O_3 are added to such a solution. In particular, such nuclei reduce the temperature for the formation of the α -modification during the subsequent thermal treatment. Suitable nuclei are very finely disperse corundum, diaspore or hematite. Very finely disperse α - Al_2O_3 nuclei having a mean particle size of less than 0.1 μm are preferably employed. In general, from 2 to 3% by weight of nuclei, based on the resulting alumina, are sufficient.

[0016] This suspension of aluminum chlorohydrate and nuclei is then evaporated to dryness and subjected to a thermal treatment (calcination). This calcination is effected in apparatuses suitable for this purpose, for example in sliding-bat furnaces, chamber furnaces, tube furnaces, rotary kilns or

microwave ovens or in a fluidized bed reactor. According to one variant of the process according to the invention, it is also possible to adopt a procedure in which the aqueous suspension comprising aluminum chlorohydrate and nuclei is injected directly into the calcination apparatus without prior removal of the water.

[0017] The temperature for the calcination should not exceed 1100° C. The lower temperature limit is dependent on the desired yield of nanocrystalline corundum, on the desired residual chlorine content and on the content of nuclei. The corundum formation begins at as low as about 500° C. but, in order to keep the chlorine content low and the yield of nanocrystalline corundum high, it is preferable to work at from 700 to 1100° C., in particular at from 1000 to 1100° C.

[0018] The time for the calcination is in general less than 30 minutes, preferably from 0.5 to 10, in particular from 0.5 to 5, minutes. Even after this short time, a sufficient yield of nanocrystalline corundum can be achieved under the abovementioned conditions for the preferred temperatures.

[0019] During the calcination, agglomerates of nanocrystalline corundum are obtained in the form of virtually spherical primary crystallites, the term "nanocrystalline" being understood as meaning a particle size of in general from 20 to 100 nm. For obtaining these primary particles, the agglomerates are comminuted by wet or dry milling, preferably by wet milling in water, for example in an attritor mill, air-jet mill or stirred ball mill. These agglomerates are deagglomerated in a subsequent step, it being possible to use all deagglomeration methods known in ceramics, since in the present case the agglomerates are ones which can be relatively easily destroyed. Wet or dry milling is preferably carried out for the deagglomeration, the wet milling preferably being effected in an attritor while the dry milling is carried out in an air-jet mill. Since the nanoparticles strived for as a product in the milling are extremely reactive, additives which prevent reagglomeration of the nanoparticles are preferably added before or during the milling. It is therefore particularly advantageous to carry out the subsequent deagglomeration in the form of wet milling. Vibration mills, attritors, ball mills, stirred ball mills or similar apparatuses are suitable for the wet milling. The use of stirred ball mills has been found to be particularly advantageous. The duration of milling depends on the strength of the agglomerates themselves and, in the process according to the invention, is usually from 2 to 6 hours. The wet milling or deagglomeration is advantageously carried out in an aqueous medium but it is also possible to use alcoholic or other organic solvents. Thus, for example after milling for two hours in water, an aqueous suspension of nanocrystalline corundum having a d50 value of less than 100 nm is obtained. During the wet milling, it is also advantageous additionally to use additives which become attached to the surface of the particles and prevent agglomeration even during a subsequent drying step. Suitable materials for this purpose are polyvinyl alcohols, stearates, wax emulsions, acrylates or polyethylene glycols. The suspension obtained after the wet milling can be converted into a defined powder by spray-drying, fluidized-bed drying or granulation.

[0020] The process according to the invention makes it possible, starting from a commercially available raw material, to produce nanocrystalline corundum in a very much shorter time compared with the processes according to the prior art.

[0021] The nanocrystalline corundum thus produced can be used in a multiplicity of applications, for example for the production of ceramic or of abrasives.

EXAMPLES

Example 1

[0022] 2% of crystallization nuclei of a suspension of very fine corundum were added to a 50% strength aqueous solution of aluminum chlorohydrate.

[0023] After the solution was homogenized by stirring, drying is effected in a rotary evaporator. The solid aluminum chlorohydrate was comminuted in a mortar, a coarse powder forming.

[0024] The powder was calcined in a muffle furnace at 1050° C. The contact time in the hot zone was not more than 5 min. A white powder whose particle distribution corresponded to the feed material was obtained.

[0025] An X-ray structure analysis shows that it is a single-phase α -alumina.

[0026] The images of the SEM (scanning electron micrograph) produced showed crystallites in the range 10-100 nm. The residual chlorine content was only a few ppm.

Example 2

[0027] The solid aluminum chlorohydrate with 2% crystallization nuclei from example 1 was fed to a laboratory rotary kiln. In this example, too, single-phase α -alumina forms in a contact time of not more than 5 minutes and at a temperature of 1050° C.

[0028] The other properties of the powder obtained are identical to the product from example 1.

Example 3

[0029] 150 g of corundum powder from example 1 were suspended in 150 g of water. The suspension was fed to a vertical stirred ball mill from Netzsch (type PE 075). The milling beads used consisted of zirconium oxide (stabilized with yttrium) and had a size of 0.3-0.5 mm.

[0030] The particle distribution of the feed material was 20-100 μ m. After respectively one, two, three and four hours, the mill was stopped and a sample was taken. In addition, the pH was checked at these times. The pH which increases with progressive deagglomeration was kept at pH 5 by addition of dilute hydrochloric acid. The samples taken hourly were characterized by means of a Horiba particle sizer.

[0031] It was found that the primary crystallites had agglomerated only slightly after 4 h. The coarse primary particles (20-100 μ m) were almost completely destroyed after only 1 h, so that a d50 of 270 nm was detectable after this time. The d50 after 4 h was <108 nm.

Example 4

[0032] For this example, an acrylate polymer (Dispex® A40, Ciba) was used for stabilizing the nanoparticles, instead of hydrochloric acid.

[0033] 150 g of corundum powder from example 1 were suspended in 150 g of water. In addition, 1 % of Dispex A40, based on the mass of corundum, was mixed with the suspension. The suspension was fed to a vertical stirred ball mill from Netzsch (type PE 075). The milling beads used consisted of zirconium oxide (stabilized with yttrium) and had a size of 0.3-0.5 mm.

[0034] The particle distribution of the feed material was 20-100 μm . After respectively one, two, three and four hours, the mill was stopped and, depending on the viscosity of the suspension, further Dispex A40 was added so that the final content was about 4%. The suspension had a d50 of 148 nm after 4 h.

Example 5

[0035] The wax emulsion Licowax® KST (Clariant) was added to the suspension from example 3 with stirring, the proportion of wax, based on the corundum, being about 3%. The dispersion thus obtained was spray-dried in a laboratory dryer from Büchi (Mini Spray Dryer B-290). The air inlet temperature was 180° C. and the temperature of the exit air was 100° C. A loose spray powder which can be used for processing comprising shaping in the area of ceramics and abrasives was obtained.

1. A process for producing nanocrystalline Al_2O_3 , comprising the steps of adding a crystallization nuclei to aluminum chlorohydrate, thermally treating the combined crystallization nuclei and aluminum chlorohydrate for less than 30 minutes to form agglomerates, and comminuting the agglomerates.

2. The process as claimed in claim 1, wherein the aluminum chlorohydrate is a compound having the chemical formula $\text{Al}_2(\text{OH})_x\text{Cl}_y$, wherein x is a number from 2.5 to 5.5 and y is a number from 3.5 to 0.5, and wherein the sum x+y is always 6.

3. The process as claimed in claim 1, wherein the crystallization nuclei is very finely dispersed $\alpha\text{-Al}_2\text{O}_3$, hematite or diaspor.

4. The process as claimed in claim 3, wherein the very finely dispersed $\alpha\text{-Al}_2\text{O}_3$ crystallization nuclei has a mean particle size of less than 0.1 μm .

5. The process as claimed in claim 1, wherein an aqueous suspension comprising aluminum chlorohydrate plus crystallization nuclei is first dried and the dried product is then calcined.

6. The process as claimed in claim 1, wherein the thermally treating step is carried out in a sliding-bat furnace, chamber furnace, tube furnace, rotary kiln, microwave oven or in a fluidized-bed reactor.

7. The process as claimed in claim 1, wherein the thermally treating step is carried out at temperatures below 1110° C.

8. The process as claimed in claim 1, wherein the thermally treating step is carried out at from 700 to 1110° C.

9. The process as claimed in claim 1, wherein an aqueous suspension comprising aluminum chlorohydrate and nuclei is injected directly into the calcination apparatus without prior removal of the water.

10. The process as claimed in claim 1, wherein the thermally treating step is carried out in from 0.5 to 30 minutes.

11. The process as claimed in claim 1, wherein the agglomerates are comminuted by wet or dry milling.

12. The process as claimed in claim 1, wherein the agglomerates are comminuted by wet milling to form a suspension, and wherein at least one additive selected from the group consisting of acrylates, polyvinyl alcohols, polyethylene glycols, stearates and wax emulsions is added during or after the wet milling.

13. The process as claimed in claim 1, wherein the agglomerates are comminuted by wet milling to form a suspension, and the suspension is spray-dried.

14. The process as claimed in claim 1, wherein the thermally treating step is carried out in from 0.5 to 10 minutes.

15. The process as claimed in claim 1, wherein the thermally treating step is carried out in from 2 to 5 minutes.

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