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(54) Title: METHODS OF REMOVING CARBON DIOXIDE THROUGH PRODUCTION OF CALCIUM CARBONATE AND CONTROLLING CRYSTAL STRUCTURE OF CALCIUM CARBONATE

(57) Abstract: This invention relates to a method of removing carbon dioxide through production of calcium carbonate by hydrating carbon dioxide and precipitating calcium carbonate, and to a method of controlling precipitation of calcium carbonate using a basic buffer upon hydration. In a process of precipitating calcium carbonate, the type of buffer is controlled upon hydration of carbon dioxide, thus controlling the morphology of precipitated calcium carbonate. Through the process of precipitating calcium carbonate, a basic buffer is adjusted, thus variously controlling the morphology of precipitated calcium carbonate.



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Description

Title of Invention: METHODS OF REMOVING CARBON DIOXIDE THROUGH PRODUCTION OF CALCIUM CARBONATE AND CONTROLLING CRYSTAL STRUCTURE OF CALCIUM CARBONATE

Technical Field

- [1] The present invention relates to a method of producing calcium carbonate, which includes hydrating carbon dioxide and precipitating calcium carbonate with the hydrated carbon dioxide, and, more particularly, to a method of controlling precipitation of calcium carbonate using a basic buffer upon hydration.

Background Art

- [2] From now on emissions of carbon dioxide causing global warming are going to be compulsorily cut. For emission thereof, a carbon tax will be paid, and thereby a considerable carbon market is expected to be formed. Because large petrochemical plants or steam power plants emit a large amount of high-concentration carbon dioxide, attempts have been made to reduce carbon dioxide emissions through changing energy sources and increasing efficiency of plants or facilities in which carbon dioxide may be relatively easily treated. Also, in order to remove carbon dioxide, storage after dissolution in water in large plants, compressive storage in the deep sea, tunnel storage, storage using photosynthesis by seaweed and storage through precipitation of calcium carbonate are under active study. In addition to the reduction of carbon dioxide emissions, removal of carbon dioxide from the air is also regarded as important and its research is being thoroughly conducted.
- [3] The safest method of storing carbon dioxide includes the use of a metal oxide so that a reaction between a metal ion and a carbonate ion obtained by dissolving carbon dioxide in water is promoted, thus immobilizing carbon dioxide. Reactions 1 and 2 below show hydration of carbon dioxide and production of calcium carbonate, as is well known in the art.
- [4] Reaction 1
- [5] $\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+ \leftrightarrow \text{CO}_3^{2-} + 2\text{H}^+$
- [6] Reaction 2
- [7] $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3$
- [8] As shown in Reaction 1, carbon dioxide is hydrated, thus producing a bicarbonate ion (HCO_3^-) and a carbonate ion (CO_3^{2-}). In particular, as the reaction progresses forward, the carbonate ion is produced in a large amount and thus reacts with the metal

ion, namely, the calcium ion. As such, in order to more rapidly induce hydration of carbon dioxide and precipitation, the forward reaction must progress.

- [9] As one method for promoting the hydration, the use of carbonic anhydrase has been proposed. This enzyme, which is present in almost all animals and plants, is reported to be a catalyst for mediating hydration and dehydration of carbon dioxide, thus promoting the hydration of carbon dioxide at a rate of 10^6 CO₂/s. Despite this capability, however, this enzyme is expensive and very difficult to be used. In fundamental experiments using this enzyme, no drastic increase in precipitation of calcium carbonate can be discerned.
- [10] Also, hydration of carbon dioxide rapidly acidifies the solution to thus inhibit additional production of the carbonate ion. Accordingly, in order to induce the forward reaction, a solution having a high pH must be used or a process of removing protons generated in hydration reaction must be performed (Proc. Nat. Acad. Sci. 70, 1986-1989, 1973).
- [11] To increase the pH, an alkaline solution may be used. However, the use of the alkaline component may undesirably increase pollution. Also, alkali metal competes with the calcium ion, causing the reduction of the precipitation rate, which is disadvantageous from the industrial point of view (J. Crystal Growth 133, 13-22, 1993).
- [12] To remove protons generated in hydration reaction, various absorbents have been developed. Korean Patent No. 836709, granted to Korea Institute of Energy Research, discloses the use of ammonia water as an absorbent in lieu of an amine-based absorbent in a gas mixture containing carbon dioxide. Korean Patent No. 650556, granted to Posco, Korea, discloses a method of adjusting the concentration of ammonia water used in an absorption tower. However, in the case of such an amine-based absorbent or ammonia, the recovery thereof is difficult. Further, ammonia is problematic because it easily evaporates even at room temperature.
- [13] In addition, adsorption or membrane separation methods have been devised. The adsorption method consumes much energy to carry out the absorption process, and to increase the absorption volume and is thus difficult to commercialize, while the membrane separation method may reduce energy but is employable in a small scale apparatus, and is thus difficult to apply to a large scale emission apparatus.
- [14] Meanwhile, calcium carbonate has the three crystal structures of calcite, aragonite, and vaterite. Among them, calcite is the most stable and is present in the largest amount in the skeleton of organisms and in nature. Aragonite, which is also less stable than calcite, is present in a large amount in organisms and in nature. Vaterite is unstable and it is reported to be rarely present in nature and organisms. In particular, the growth of aragonite crystals requires a narrow range of special conditions, and thus it is known that this structure is considerably difficult to grow in laboratory (Tai, C. Y., Chen, F.

B. AICHE Journal, 44(8), 1790-1798 1998, Hu, Z., Deng, Y., J. Colloid Interface Sci. 266, 359-365, 2003). Generally, aragonite has an acicular structure which grows to become very long in the direction of longitudinal axis, and a great amount of energy is required to break crystals thereof but the crystal size is not large. On the other hand, calcite grows to form crystals of a large size but these crystals are easy to break. Calcium carbonate in the acicular structure of aragonite having a high aspect ratio (length/width ratio) is important as a filler for improving mechanical strength in the rubber or plastic industries (W. Shang, Q. Liu, B. Liu, L. Chen, S. Chen, Proceedings of 1998 International Symp. On Electrical Insulating Materials, 595-598, 1998).

- [15] Therefore, the demand for methods able to control the precipitation of calcium carbonate through hydration of carbon dioxide is ever present.

Disclosure of Invention

Technical Problem

- [16] Accordingly, the present invention provides a method of absorbing carbon dioxide from the air into an aqueous solution containing a basic buffer and a calcium ion, thus inducing precipitation of calcium carbonate, thereby removing carbon dioxide from air, and also provides a method of controlling the crystal structure of calcium carbonate, including a spherulite coating structure, a platelet structure or a long cylindrical structure having a high aspect ratio.

Solution to Problem

- [17] An aspect of the present invention provides a method of removing carbon dioxide, including hydration carbon dioxide in a solution containing a basic aqueous polymer and a calcium ion, and selectively carbonic anhydrase or polyacrylic acid, thus precipitating calcium carbonate.
- [18] In the present invention, carbon dioxide may be hydrated in a solution containing an aqueous polymer having an amine group, and the hydrated carbon dioxide may react with the calcium ion contained in the solution so that calcium carbonate is precipitated, thereby removing carbon dioxide. The precipitated amount, the precipitation rate, and the precipitated location may vary according to a carbonic anhydrase or polyacrylic acid which is selectively contained in the solution, and also, the crystal structure may change.
- [19] In the present invention, in the case where carbon dioxide is hydrated in the solution containing the basic aqueous polymer and the calcium ion to thus precipitate calcium carbonate, the precipitated calcium carbonate has an acicular aragonite crystal structure.
- [20] In an embodiment of the present invention, as the aqueous polymer having an amine group, particularly useful is polyalkyleneimine having a weight average molecular

weight of 200~750,000 and preferably 400~25,000. The aqueous polymer having an amine group may be used at a concentration of about 1~30 mg/ml. Examples of polyalkyleneimine include polyethyleneimine, polypropyleneimine and so on.

- [21] In the embodiment of the present invention, polyalkyleneimine may be reused after the absorbed hydrogen ion is desorbed. Preferably, polyalkyleneimine is recycled by passing it through a solution containing hydrated carbon dioxide, and more preferably, is used in a state of being immobilized to a column or beads so as to facilitate the recycling thereof.
- [22] In the present invention, carbon dioxide is hydrated in the solution containing the basic aqueous polymer, the carbonic anhydrase and the calcium ion, and thus calcium carbonate is precipitated.
- [23] In the present invention, carbonic anhydrase which is an enzyme present in almost all animals and plants is reported to be a catalyst for mediating hydration and dehydration of carbon dioxide. In an aqueous calcium chloride solution containing a small amount of carbonic anhydrase and polyethyleneimine, carbon dioxide may be initially drastically hydrated, and also calcium carbonate may be precipitated in the form of a film at the interface between the solution and air.
- [24] In the present invention, carbonic anhydrase may be used at a concentration of 1~30 $\mu\text{g/ml}$.
- [25] As for the above film crystals, calcium carbonate is conventionally obtained in the form of vaterite and calcite crystals in a closed system using ammonium carbonate. In the predetermined experimental apparatus, aragonite or calcite crystal structures may be obtained directly using carbon dioxide of air. The acicular crystals are observed using an electron microscope, and may be confirmed to be aragonite through X-ray diffraction. The aragonite crystals may partially include calcite crystals, and the amount of calcite crystals may vary depending on the molecule weight of polyethyleneimine (PEI). These results are similar to when mainly producing calcite and aragonite in nature and in organisms. In the embodiment of the present invention, carbonic anhydrase may include various enzyme derivatives. Particularly useful is bovine carbonic anhydrase (BCA).
- [26] In the present invention, carbon dioxide may be removed by hydrating carbon dioxide in a solution containing the aqueous polymer having an amine group, the polyacrylic acid and the calcium ion, and selectively carbonic anhydrase, thus precipitating calcium carbonate.
- [27] In the process of producing calcium carbonate like the present invention, to control the crystal structure, polyacrylic acid (PAA) having an acidic group may be used (Han, J. T., Xu, X., Kim, D. H & Cho, K. Adv. Funct. Mater. 15, 475-480, 2005). This polyacrylic acid is mainly used as an additive for function of an acidic protein in

biomineralization and is well known to inhibit a crystallization reaction of calcium carbonate.

[28] In the present invention, polyacrylic acid may have a molecular weight ranging from 200 g/mole to 100,000 g/mole, and preferably from 1,000 g/mole to 10,000 g/mole.

[29] In an embodiment of the present invention, in the case where polyacrylic acid is added to the solution containing polyethyleneimine, calcium ion and carbonic anhydrase to induce precipitation, calcium carbonate is more highly precipitated at the interface between the solution and air than on a bottom of a vessel, and precipitation behavior may be controlled by the concentration of polyacrylic acid.

[30] In an embodiment of the present invention, as observed using an electron microscope, in the case where polyethyleneimine (having a molecular weight of 400 and containing primary, secondary and tertiary amines) is used at a concentration of 10 mg/ml or more, a coating form in which the film is completely spread on the interface may be exhibited.

[31] In another embodiment of the present invention, in the case where polyacrylic acid is used at a concentration of 10 $\mu\text{g/ml}$, tabular calcite crystals may be formed, and in the case where polyacrylic acid is used at a concentration of 50 $\mu\text{g/ml}$ or more, calcite in a cylindrical fiber form having a diameter of 100~200 nm with a high aspect ratio may be produced.

[32] In the present invention, the polyalkyleneimine aqueous polymer may be used alone as a buffer for removing protons or may be used in combination with a conventional basic buffer such as ammonium hydroxide or Tris. Also, a hydration enzyme such as bovine carbonic anhydrase (BCA) may be further included.

[33] In the present invention, the calcium ion is used to react with the hydrated carbon dioxide in order to precipitate calcium carbonate. Any product may be used as long as it supplies the calcium ion. For example, calcium or calcium-containing limewater or seawater may be used.

[34] Another aspect of the present invention provides a novel industrial method using the process of precipitating calcium carbonate from carbon dioxide using an aqueous polymer having an amine group. For example, ceramic coating in the plastic is studied to improve surface hardness for optical purposes, add optical and magnetic components, and prevent flooding and aging. The nano-rod has various applications in addition to the filler.

Advantageous Effects of Invention

[35] According to the present invention, in the production of calcium carbonate using carbon dioxide, a novel method of controlling crystallization behavior of calcium carbonate, for example, crystallization rates, crystal content, crystal morphology, and

crystal positions can be provided.

Brief Description of Drawings

- [36] FIG. 1 is a photograph of calcium carbonate precipitated using 100 mM Tris and 10 mM CaCl_2 .
- [37] FIG. 2 is a photograph of calcium carbonate precipitated using 100 mM ammonium and 10 mM CaCl_2 .
- [38] FIG. 3 is a photograph of calcium carbonate precipitated using 10 mg/ml PEI2 and 10 mM CaCl_2 .
- [39] FIG. 4 is a photograph of calcium carbonate precipitated using 20 mg/ml PEI0.4, 10 $\mu\text{g/ml}$ PAA and 10 $\mu\text{g/ml}$ BCA.
- [40] FIG. 5 is a photograph of calcium carbonate precipitated using 10 mg/ml PEI2.0, 50 $\mu\text{g/ml}$ PAA and 10 $\mu\text{g/ml}$ BCA.
- [41] FIG. 6 is a photograph of calcium carbonate precipitated using 10 mg/ml PEI2.0, 10 $\mu\text{g/ml}$ PAA and 10 $\mu\text{g/ml}$ BCA.

Mode for the Invention

- [42] A better understanding of the present invention may be obtained through the following examples which are set forth to illustrate, but are not to be constructed as limiting the present invention.
- [43] Samples
- [44] PEI0.4: polyethyleneimine having a molecular weight of 400 and containing primary, secondary and tertiary amines, available from Sigma Aldrich
- [45] PEI0.8: polyethyleneimine having a molecular weight of 800 and containing primary, secondary and tertiary amines
- [46] PEI1.3: polyethyleneimine having a molecular weight of 1,300 and containing primary, secondary and tertiary amines
- [47] PEI2: polyethyleneimine having a molecular weight of 2,000 and containing primary, secondary and tertiary amines
- [48] PEI25: polyethyleneimine having a molecular weight of 25,000 and containing primary, secondary and tertiary amines
- [49] PEI750: polyethyleneimine having a molecular weight of 750,000 and containing primary, secondary and tertiary amines
- [50] 10 mM aqueous CaCl_2
- [51] Bovine carbonic Anhydrase (BCA), available from Sigma Aldrich
- [52] Polyacrylic acid (PAA)
- [53] Comparative Example
- [54] While 50 ml of 10 mM aqueous CaCl_2 was used, cases where a basic buffer was not used with addition of BCA and where aqueous ammonium (ammonium hydroxide) or

Tris (tris(hydroxyethyl)aminomethane) was used in lieu of PEI as the basic buffer, with or without addition of BCA, were tested. The samples were placed in a Petri dish having a diameter of 10 cm, stirred at about 300 rpm for about 10 hours using a magnetic stirrer in a state of being exposed, and then allowed to stand. Then, the 24-hour cumulative precipitation amount was measured. when all calcium ions in the solution was consumed and completely converted into calcium carbonate, the theoretical amount of CaCO_3 would be 50 mg.

[55] Table 1

[Table 1]

[Table]

Use of No PEI Buffer

Basic Buffer (mM)	CaCl_2 (mM)	BCA ($\mu\text{g/ml}$)	Precipitation of CaCO_3 after 24 hours		Film Formation	Crystal Structure
			Amount (mg)	Calcium Consumption (%)		
-	10	-	0	0	X	
-	10	10	0	0	X	
Ammonium, 100	10	-	27	52	X	Aragonite
Ammonium, 100	10	10	27	52	X	Aragonite
Tris, 100	10	-	32	61	X	Aragonite
Tris, 100	10	10	36	69	X	Aragonite

[56] Example 1

[57] 50 ml of an aqueous solution containing 10 mM CaCl_2 and 10 mg/ml PEI basic buffer was placed in the Petri dish having a diameter of 10 cm, stirred at about 300 rpm for about 10 hours using a magnetic stirrer in a state of being exposed. Then, the 24-hour cumulative CaCO_3 precipitation amount was measured.

[58] Table 2

[Table 2]

[Table]

Use of PEI Buffer without addition of BCA

Basic Buffer, (mg/ml)	CaCl ₂ (mM)	BCA (μ g/ml)	Precipitation of CaCO ₃ after 24 hours		Film Formation	Crystal Structure
			Amount (mg)	Calcium Con- sumption (%)		
PEI0.4, 10	10	-	47	86	X	Aragonite, acicular
PEI0.8, 10	10	-	39	85	X	Aragonite, acicular
PEI1.3, 10	10	-	43	86	X	Aragonite, acicular
PEI2.0, 10	10	-	42	88	X	Aragonite, acicular
PEI25, 10	10	-	48	77	X	Aragonite, acicular
PEI750, 10	10	-	40	77	X	Aragonite, acicular

[59] Example 2

[60] Table 3

[Table 3]

[Table]

Use of PEI Buffer with addition of BCA

Basic Buffer, (mg/ml)	CaCl ₂ (mM)	BCA (μ g/ml)	Precipitation of CaCO ₃ after 24 hours		Film Formation	Crystal Structure
			Amount (mg)	Calcium Consumption (%)		
PEI0.4, 10	10	10	47	90	○	Aragonite, acicular
PEI0.8, 10	10	10	39	75	○	Aragonite, acicular
PEI1.3, 10	10	10	43	82	○	Aragonite, acicular
PEI2.0, 10	10	10	42	81	○	Aragonite, acicular
PEI25, 10	10	10	48	92	○	Aragonite, acicular
PEI750, 10	10	10	40	77	○	Aragonite, acicular

[61] As is apparent from the above results, the precipitation amount was evaluated to be insignificant without the use of basic buffer. In the case where ammonia or Tris was used as the basic buffer, 50% or more of calcium carbonate was precipitated following an aging time of 24 hours. When ammonium or Tris was used, an acicular structure was slightly formed following an initial aging time of about 5 hours, whereas acicular aragonite was mostly produced following an aging time of 24 hours, as shown in FIGS. 1 and 2. When BCA was added thereto, the precipitation rate was slightly increased even following an aging time of 24 hours but was not so high. Upon use of PEI, the calcium consumption was 75% or more, namely, the precipitation rate was very high. When PEI was used, the ratio of acicular structure was higher, and the acicular aragonite crystal structure could be seen to be formed following an aging time of about 5 hours (FIG. 3).

[62] Example 3

[63] Table 4

[Table 4]

[Table]

Use of PEI buffer with addition of BCA and PAA

Basic Buffer, (mg/ml)	CaCl ₂ (mM)	BCA (μ g/ml)	PAA (μ g/ml)	Calcium Consumption (%)		Film Formation	Crystal Structure
				After 24 hours	After 130 hours		
PEI0.4, 10	10	10	10	82	86	○	Calcite, coating
PEI0.4, 20	10	10	10	82	86	○	Calcite, coating
PEI0.4, 30	10	10	10	82	86	○	Calcite, coating
PEI0.4, 10	10	10	50	38	76	○	Calcite, cylindrical rod
PEI0.4, 10	10	10	100	0	76	○	Calcite, cylindrical rod
PEI2.0, 10	10	10	10	38	76	○	Calcite, coating
PEI2.0, 10	10	10	50	0	80	○	Calcite, cylindrical rod
PEI2.0, 10	10	10	100	0	57	○	Amorphous

[64] As shown in FIG. 4, calcium carbonate crystals in a coated form were produced when used 10 mg/ml or more PEI0.4 and 10 μ g/ml or less PAA. Also, when PAA was used at a concentration of 30 μ g/ml or more, cylindrical nano-sized calcium carbonate rods were formed (FIG. 5). Also, when 10 mg/ml PEI2.0 and 10 μ g/ml PAA were used, platelet calcium carbonate was precipitated (FIG. 6).

Claims

- [Claim 1] A method of removing carbon dioxide, comprising hydration of carbon dioxide in a solution containing an aqueous polymer having an amine group and a calcium ion, thus precipitating calcium carbonate.
- [Claim 2] The method according to claim 1, wherein the calcium carbonate has an acicular aragonite crystal structure.
- [Claim 3] The method according to claim 1, wherein the aqueous polymer having an amine group is polyalkyleneimine having a weight average molecular weight ranging from 400 to 750,000.
- [Claim 4] The method according to claim 3, wherein the polyalkyleneimine has a weight average molecular weight ranging from 400 to 25,000.
- [Claim 5] The method according to claim 1, wherein the aqueous polymer having an amine group is used at a concentration of 1~50 mg/ml.
- [Claim 6] The method according to claim 1, wherein the aqueous polymer having an amine group is recycled by immobilizing it to a column or beads and passing it through a solution containing hydrated carbon dioxide.
- [Claim 7] A method of removing carbon dioxide, comprising hydration of carbon dioxide in a solution containing an aqueous polymer having an amine group, carbonic anhydrase and a calcium ion, thus producing calcium carbonate.
- [Claim 8] The method according to claim 7, wherein the calcium carbonate is formed into a film at an interface between air and the solution.
- [Claim 9] The method according to claim 8, wherein the film has an acicular aragonite crystal structure.
- [Claim 10] The method according to claim 7, wherein the aqueous polymer having an amine group is polyalkyleneimine.
- [Claim 11] The method according to claim 7, wherein the carbonic anhydrase comprises a hydration enzyme including bovine carbonic anhydrase.
- [Claim 12] A method of removing carbon dioxide, comprising hydration of carbon dioxide in a container of a solution containing an aqueous polymer having an amine group, polyacrylic acid and a calcium ion, and selectively, carbonic anhydrase, thus producing calcium carbonate.
- [Claim 13] The method according to claim 12, wherein the calcium carbonate is precipitated in a larger amount at the air/solution interface than on a bottom of the vessel.
- [Claim 14] The method according to claim 12, wherein the aqueous polymer having an amine group comprises polyethyleneimine and is used at a

concentration of 1~50 mg/ml.

[Claim 15] The method according to claim 14, wherein the polyacrylic acid is used at a concentration of 1~500 $\mu\text{g/ml}$.

[Claim 16] The method according to claim 12, wherein the calcium carbonate has a film crystal structure when the concentration of the polyacrylic acid is 10 $\mu\text{g/ml}$ or less.

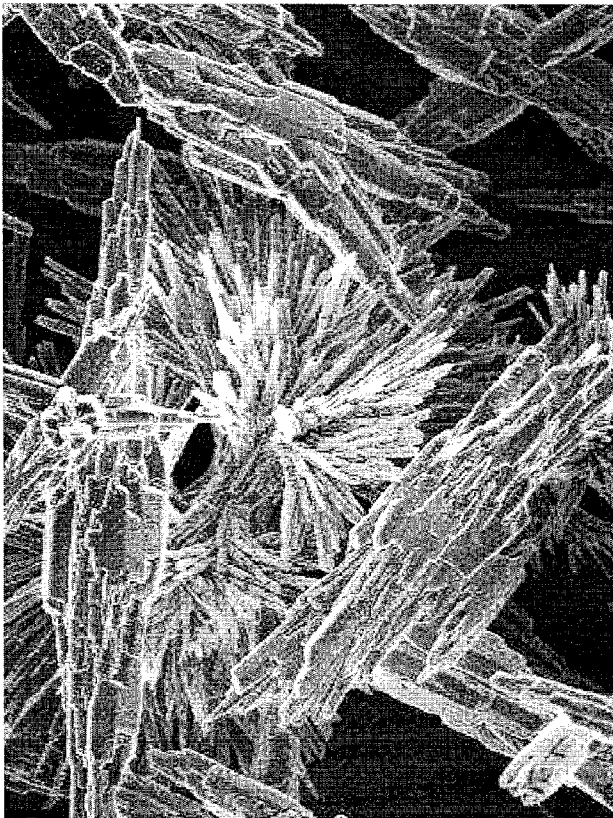
[Claim 17] The method according to claim 15, wherein a cylindrical calcite crystal structure having a diameter of 50~200 nm is formed when the concentration of the polyacrylic acid is maintained at 50~500 $\mu\text{g/ml}$.

[Claim 18] A method of producing calcium carbonate comprising hydration of carbon dioxide in a solution containing a basic buffer and a calcium ion, thus precipitating calcium carbonate, wherein precipitation of calcium carbonate is controlled using carbonic anhydrase and/or polyacrylic acid.

[Fig. 1]



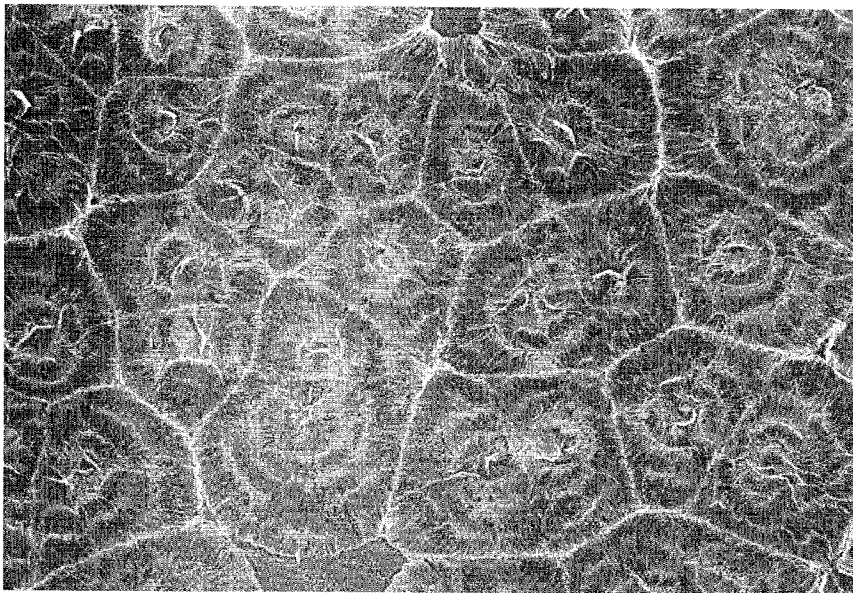
[Fig. 2]



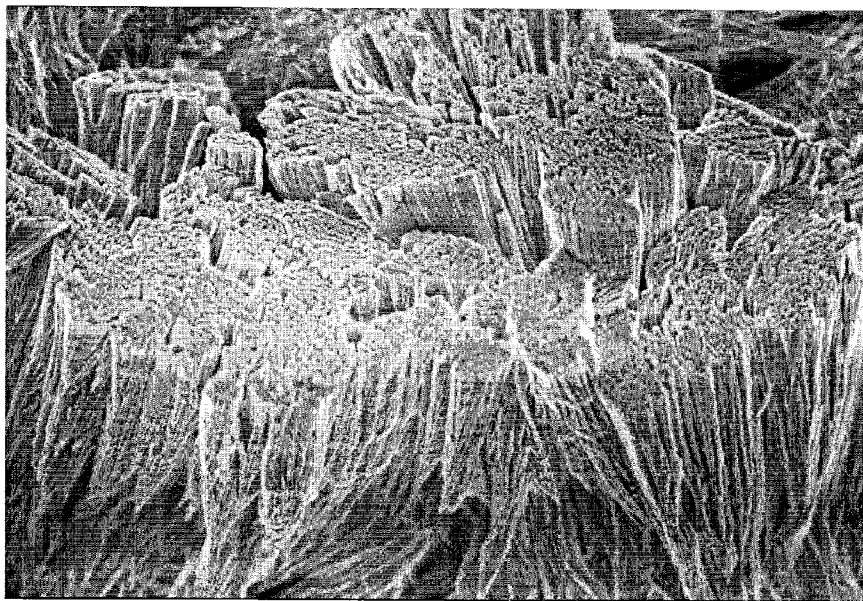
[Fig. 3]



[Fig. 4]



[Fig. 5]



[Fig. 6]

