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METHOD OF GROWING ALPHA-ALUMINA SINGLE CRYSTAL RIBBONS

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Fig. 1.

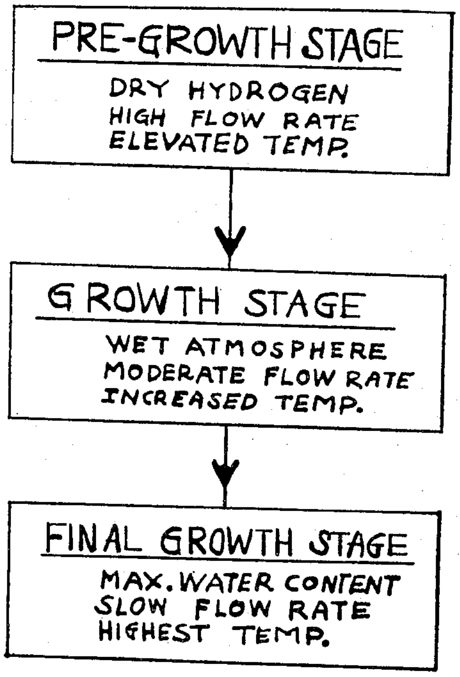
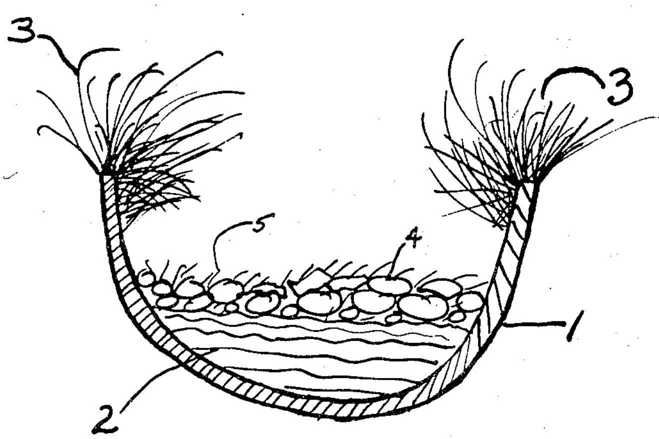


Fig. 2.



INVENTORS
JAMES J. SHYNE
JOHN V. MILEWSKI

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METHOD OF GROWING ALPHA-ALUMINA SINGLE CRYSTAL RIBBONS

James J. Shyne, Caldwell, and John V. Milewski, Saddle Brook, N.J., assignors to General Technologies Corporation, Reston, Va., a corporation of Delaware

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U.S. Cl. 23—142 12 Claims
Int. Cl. C01f 7/42

ABSTRACT OF THE DISCLOSURE

A new ribbon form of single crystal alpha-alumina is described. This form is characterized by advantageous crystallographic and geometrical properties. An improved process is described for making such a product in high yield during a short growth period. The process involves periodically increasing the water concentration of hydrogen gas passed over a melt of aluminum during growth of the ribbons. A ceramic receptacle of predetermined composition and made under certain firing conditions is described for holding the aluminum melt during the process.

This invention relates to alpha-alumina single crystals, and more particularly, to a method of making ribbons of such material in high yield.

This application is a continuation of application Ser. No. 373,982, filed June 10, 1964, by James J. Shyne and John V. Milewski and now abandoned.

Single crystals of alpha-alumina, otherwise known as sapphire, in the form of extremely fine fibers, or whiskers, are known in the art to possess unusually high strengths. For example, such sapphire whiskers have been shown to possess tensile strengths of from two to four million p.s.i. This property makes the material extremely desirable for reinforcing structural materials, such as metal and plastic. Alpha-alumina whiskers have been grown by passing hydrogen gas containing a small amount of water over molten aluminum to form a volatile lower aluminum oxide. Thereafter the vaporous aluminum oxide is condensed at a lower temperature onto a substrate whereupon it disproportionates into aluminum and single crystal fibers of alpha-alumina.

At the conclusion of the run, a portion of the aluminum charge also is oxidized to bulk alumina. This by-product material generally is present in the form of cluster balls over the residue of the aluminum charge. The desired fibrous alpha-alumina is found among these cluster balls and must be separated therefrom. Not only is the yield of fibrous material in a given batch small, but the isolatable amount is even smaller. Thus, lack of available material has retarded commercial utilization of alpha-alumina whiskers.

Accordingly, it is an object of the present invention to provide a method of making alpha-alumina single crystals in high yield.

Another object of this invention is to provide a method of growing single crystal alpha-alumina in the form of ribbons substantially out of contact with other growth products.

These and other objects of the invention will be made apparent from the following more particular description of the invention.

In general, the method of the present invention includes first providing an aluminum source material in a refractory receptacle, preferably composed of a fired-intimate mixture of particles comprising alumina and finely-divided aluminum metal. The aluminum content is usually between about 1 to 20% by weight of the receptacle. The re-

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ceptacle containing the aluminum charge then is placed in a furnace at a temperature between about 2200° and 3500° F., whereupon a melt of aluminum is produced. Thereupon the melt is contacted with a predetermined concentration of water vapor in a hydrogen gas atmosphere. The water concentration and flow rate of the gas is adjusted in a predetermined manner during various stages of the run. Alpha-alumina single crystals in ribbon form then is deposited in high yield on the walls and edges of the receptacle. Since the ribbons are formed substantially out of contact with by-products formed during the run, it can be readily provided in isolated form.

In accordance with the invention, the course of the growth of the alpha-alumina ribbons is controlled by a number of parameters, particularly the composition of the receptacle, the amount of moisture in the hydrogen gas over the aluminum charge, the rate of flow of the hydrogen gas stream, and the temperature of the reactants, at various stages during the run. In this manner the reactants are developed at a uniform rate, and thus build-up of the ribbons takes place uniformly.

The apparatus used in the process is of standard design. This includes a tubular electric-resistance furnace to heat the charge to the molten stage, and a gas train system to supply the desired hydrogen gas stream.

In the accompanying drawings:

FIGURE 1 is a flow sheet to illustrate the process steps according to a preferred practice of the invention.

FIGURE 2 shows the formation of the desired alpha-alumina ribbons on the edges of the receptacle.

Referring now to the flow sheet of FIGURE 1, the process of the invention is illustrated wherein improved yields of alpha-alumina ribbons are obtained. The run proceeds in three stages, designated the pre-growth, growth, and final growth stages. During the pregrowth stage, the aluminum charge is wetted into the ceramic receptacle. No ribbons grow during this stage. The hydrogen over the aluminum charge is kept as dry as possible in the pre-growth stage, suitably containing no higher than 50 p.p.m. At the end of the pre-growth stage an initial burst of vaporous aluminum oxide is observed, and the stage of nucleation and growth of the ribbons commences. At this point, a substantial amount of water is added to the atmosphere above the melt, suitable up to a maximum of 40,000 p.p.m. The water preferably is added incrementally while the ribbons are growing. A maximum water concentration is present over the melt at the end stage of the run, referred to herein as the final growth stage. Preferably the water concentration is about 300 p.p.m. at the beginning of the growth stage and about 3000 p.p.m. during the final growth stage.

The pre-growth stage at the start of the run, usually takes about 10 minutes. During this stage the dry gas stream is maintained at a high rate of flow, generally between about 0.01 to 0.06 cu. ft./sec., and optically at about 0.03 cu. ft./sec. During ribbon growth, however, the hydrogen flow rate is substantially reduced relative to the initial dry gas flow rate. Preferably the rate for the early stages of growth is in the range of 0.001 to 0.03 cu. ft./sec., with 0.001 cu. ft./sec. being considered optimum. For the final stage of growth, a flow rate of 0.0001 cu. ft./sec. is preferred. The flow rates given are relative to the dimensions of the apparatus used, which are described in detail in the examples.

The temperature of the melt may be held constant during the run, as for example, between about 2200°–3500° F. However, for a high yield of ribbon product, it is preferable that the melt be heated at a steadily increasing temperature during the growth and final growth stages, preferably from about 2500° to about 3100° F., during a run of about an hour.

The yield and collectability of the desired fibers also is increased when the receptacle is of a predetermined composition. While alumina itself may be used, it is a feature of the invention that the receptacle is constructed of a fired-intimate mixture of particles comprising alumina and finely-divided aluminum metal. The aluminum particles usually are present in an amount comprising between about 1–20% by weight of the receptacle. Generally the finer the particle size of the aluminum, the lower is the amount of aluminum required in the receptacle composition. For example, at a particle size of 200 mesh, an aluminum content of 2.5–7.5% is preferred.

Usually the ceramic material used to form the receptacle includes, in addition to alumina, metal oxides such as silica and iron oxide, and to a lesser degree, titania, chromium oxide, zirconium oxide or cobalt oxide. These oxides appear to function beneficially in the process.

The manner of preparing the receptacle also is an important factor in increasing the yield of ribbons. In accordance with a preferred embodiment of the invention, the finely-divided alumina, or an alumina composition, and the aluminum powder, are mixed thoroughly and fired at an elevated temperature, preferably between about 2000°–2500° F., and optimally at about 2200° F.

The presence of aluminum metal in intimate contact with alumina in the receptacle for the aluminum charge is important to the process because such a receptacle enables the production of vaporous aluminum oxide at a more controlled rate than with an aluminum receptacle, thus providing a sustained growth step at a uniform rate.

In accordance with another feature of the invention, a small amount of alumina material is admixed with the aluminum charge, suitable between about 5–50% by weight of the charge, and preferably about 20% by weight, to still further improve the yield of ribbons.

Referring now to FIGURE 2, there is schematically illustrated the formation of the alpha-alumina single crystal ribbons on the receptable in accordance with the present invention. A receptacle **1** carries an aluminum charge **2** therein, which has been partially converted to the desired alpha-alumina product **3**. The product forms as ribbons on the edges and sides of the receptacle. Alumina cluster balls **4** are obtained as a by-product. Only a small amount of fibrous material **5** is formed on and within the cluster balls themselves.

A typical alpha-alumina single crystal product in accordance with the present invention is a ribbon of rhombohedral cross-section. The ribbon has a width to thickness ratio of between about 1:1 to 12:1, and length from 10 to 25,000 times the width. Generally the length is from about 0.5 to 4 inches, and the width is at least 0.5 micron.

The yield of ribbon material is in the order of 0.1 gram per hour per inch of exposed edge surface of the receptacle. For example, when a receptacle having an edge length of 20 inches is used, a yield of 2 g. is obtained.

The invention will now be illustrated more fully with reference to the following specific examples.

Example 1

An alumina boat having the dimensions 5 x 17 x 2 inches, and weighing about 3 lbs. 4 oz. is charged with 2.5 pounds of aluminum pellets which are spread evenly on the bottom of the boat. The boat and aluminum charge then is inserted into a furnace having a cross-sectional open area of 20 square inches. The temperature of the furnace is set at 2775° F. Purified hydrogen containing less than 20 p.p.m. of water vapor then is admitted into the furnace over the charge at a flow rate of 0.01 cu. ft./sec. for a period of about ten minutes. Thereupon a vaporous substance is produced from the charge. At this point 300 p.p.m. of water is added to the hydrogen gas stream and the flow rate is decreased to 0.001 cu. ft./sec. Ribbon formation then proceeds on the edges of the boat. After about twenty to thirty minutes, the water content of the hydrogen is increased to 3000 p.p.m. and the flow rate is decreased to 0.0001 cu. ft./sec. The total growth period is about an hour. The boat then is removed from the furnace, cooled to room temperature, and the ribbon product is isolated. The ribbons are alpha-alumina single crystals having a rhombohedral cross-section. A yield of about 0.2 g. of ribbon material is collected. The width of the ribbons average between 10–100 microns; the length about 2 inches; and the thickness about 1–25 microns.

Example 2

A boat for the aluminum charge is prepared by mixing 3 lbs. 2 oz. of alumina powder and 0.16 lb. of 200 mesh aluminum powder (5% by weight of aluminum) in a slip-casting mold. The green ceramic then is fired in air at 2200° F. for about a half-hour. The boat receptacle thus prepared is used in place of the alumina boat in Example 1 and the process of Example 1 is carried out in a similar manner with an aluminum charge. Using a boat of this composition, the yield of alpha-alumina ribbons is increased thereby to 2 g. The ribbons also are found more abundantly on the sides and walls of the boat, as represented in FIGURE 2.

Example 3

A mixture of 3 lbs. 2 oz. of ceramic powder material sold by Norton and Co. by designation "1162" having the following composition: 75 parts by weight alumina, 15 parts by weight silica, 5 parts by weight titania, 2.5 parts by weight ferric oxide and 2.5 parts by weight of other metallic oxides, and 0.16 lb. of 200 mesh aluminum powder (5% by weight of aluminum) is prepared in a slip-casting mold. The green ceramic then is fired in air at 2200° F. for about a half-hour. The boat thus prepared is used in the process described in detail in Example 1. The yield of alpha-alumina ribbons is increased thereby to about 2.5 g.

Example 4

Into the boat receptacle prepared in the manner described in Example 3 is placed a charge of 2.5 pounds of aluminum pellets. The boat and aluminum charge is placed in a furnace heated at 2775° F. Purified hydrogen containing less than 15 p.p.m. of water vapor then is admitted at a flow rate of 0.03 cu. ft./sec. for a period of about ten minutes. Then the water content of the hydrogen gas is increased to 350 p.p.m. and the flow rate is decreased to 0.001 cu. ft./sec. Concurrently the temperature of the furnace is increased, finally reaching a maximum temperature of 3100° F. at the end of the run. Growth of alpha-alumina ribbons occurs on the sides and walls of the boat. After about 20 minutes of growth, the water content of the hydrogen gas is increased to about 3000 p.p.m., and the flow rate is decreased to 0.0001 cu. ft./sec. After a total period of growth of about an hour, the ribbons are collected. The yield is 8 g. of ribbons.

Example 5

A reaction charge consisting of 2.5 pounds of aluminum pellets and 1.6 oz. of alumina chips are mixed together and placed in the boat receptacle prepared according to the manner described in Example 3. The process of Example 4 then is carried out. The ribbons thus obtained are substantially larger than those made in previous examples. Generally these ribbons are about two inches in length, and some are as long as four inches.

While the invention has been described with particular reference to certain embodiments thereof, it will be understood that changes and modifications may be made by those skilled in the art which do not depart from the spirit of the invention. It is intended to be limited only by the appended claims.

What is claimed is:

1. In a process of growing single crystal alpha-alumina ribbons by passing hydrogen and water vapor over a melt of aluminium in a ceramic receptacle whereby a volatile lower aluminum oxide is formed, thereafter condensed onto a substrate and disproportionated into aluminum and single crystal fibers of alpha-alumina, the improvement wherein a high yield of an elongated ribbon product is obtained in a short time, characterized by periodically increasing the water content of the hydrogen over the melt during the period of growth, starting from essentially dry hydrogen and being increased substantially during the run to no higher than 40,000 p.p.m.

2. The process according to claim **1** wherein the water content of the hydrogen is increased rapidly at the beginning of growth and then incrementally while the ribbons are growing.

3. The process according to claim **1** wherein the water content of the hydrogen is increased from no higher than 50 p.p.m. to about 300 p.p.m. at the beginning of growth, and then incrementally to about 3,000 p.p.m. at the end of growth.

4. The process according to claim **1** wherein the temperature of the melt is increased periodically during the run.

5. The process according to claim **1** wherein the flow rate of the hydrogen initially is rapid, and then is substantially decreased during the end of the run.

6. The process according to claim **1** wherein the ceramic receptacle contains alumina, silica, titania, iron oxide, chromium oxide, cobalt oxide or zirconium oxide.

7. The process according to claim **1** wherein the ceramic receptacle contains at least silica, titania, iron oxide, chromium oxide, cobalt oxide or zirconium oxide.

8. The process according to claim **1** wherein the ceramic receptacle contains between 1–2% by weight of finely-divided aluminum particles.

9. The process according to claim **8** wherein the ceramic receptacle is made by firing its constituents in air at a temperature of about 2200°–2500° F.

10. The process according to claim **8** wherein the aluminum content of the ceramic receptacle is about 2.5–7.5% by weight.

11. The process according to claim **1** wherein the aluminum melt is wetted into the ceramic receptacle during a pre-growth stage of the process during which no ribbons grow by passing hydrogen containing no more than 50 p.p.m. water over said melt.

12. The process according to claim **11** wherein the hydrogen during the pre-growth stage is passed over the melt at a greater flow rate and the melt is maintained at a lower temperature than during growth of the ribbons.

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OSCAR R. VERTIZ, *Primary Examiner.*

HERBERT T. CARTER, *Assistant Examiner.*