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(54) A MAT ARTICLE OF SINGLE CRYSTAL ALPHA-ALUMINA FIBERS

(71) We, GENERAL TECHNOLOGIES CORPORATION, a Corporation organised under the laws of the State of Delaware, United States of America, of 1821 Michael Faraday Drive, Reston, Virginia, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a mat article comprising interconnected groups of single crystal alpha-alumina fibers and a method of growing such a mat article.

Alpha-alumina has been prepared as single crystal fibers or whiskers. These fibers generally have a diameter in the order of microns and lengths up to several inches. For example, the following U.S.A. patent specifications describe the preparation and properties of such fibers: 3,011,870, 3,023,115, and 3,077,380. As prepared fibers appear either as individual fibers or in clusters of fibers in the form of balls, sometimes referred to as a "wool" or "cotton". In commercial uses of these fibers, however, it is advantageous to provide them in the form of a mat article.

According to the present invention there is provided a mat article comprising interconnected groups of single crystal alpha-alumina fibers, each of said groups including a plurality of said fibers connected together substantially at a common point and at least some of the fibers in each of said groups being enmeshed with the fibers in another or others of said groups to form said mat article with two opposed surfaces, the common points at which the fibers in the respective groups are connected together being spaced apart at one of said surfaces, and the other of said surfaces being substantially covered with substantially separate enmeshed fibers.

The mat thus has two opposed surfaces having distributions of fibers which differ substantially from each other, the surface wherein the fibers are enmeshed but otherwise substantially separate from each other has a greater distribution of fibers than the other surface, and the fiber mat has inherent strength as a result of the substantial number of enmeshings of fibers near one surface so that it can be handled and is reasonably durable. In compression the mat is rather resilient, probably due to its particular structure.

Another feature of the invention consists in providing a method of growing a mat article comprising interconnected groups of single crystal alpha-alumina fibers, including the steps of passing hydrogen and water vapour over a melt of aluminum in a ceramic receptacle provided with a loosely-fitting cover of ceramic material so that deposition of said fibers occurs at spaced-apart sites on the underside of said cover thereby to form enmeshed groups of said fibers wherein the fibers in each of said groups are connected together substantially at and radiate from one of said sites.

The invention, and how it may be performed, is further described below with reference to the accompanying drawings, in which by way of example:—

FIGURE 1 shows in schematic section a receptacle, cover and charge at the beginning of a "run",

FIGURE 2 illustrates the receptacle, cover, residue of charge, and mat article formed at the end of the "run",

FIGURE 3 shows the cover carrying the mat article after separation from the receptacle,

FIGURE 4 illustrates the mat article after separation from the cover,

FIGURE 5 is a top view of the same article, and

FIGURE 6 is a longitudinal view of another mat article showing secondary fibers.

FIGURE 1 shows a receptacle 1 in which is an aluminum charge 2. The receptacle is loosely fitted with a ceramic cover 3. The distance between the top of the charge 2 and the bottom of the cover 3 will affect the density or porosity of the mat obtained. A shorter distance of separation will result in a denser mat, while a longer separation will produce a less dense or looser mat. Generally a separation of less than 1/2 inch, preferably about 1/4 inch, will produce a mat having a bulk density of about 2 to 5 times greater than that obtained with a separation of about 3/4 inch or more. The receptacle with its charge and cover is positioned in an elongated ceramic tube (not shown) which is placed in a suitable electric resistance furnace capable of attaining temperatures sufficient to melt the charge. A gas-circulating system is connected to the ceramic tube for supplying a suitable gas carrying a predetermined water content. Within the tube some of the gas passes through the opening between the receptacle and the cover and circulates through the receptacle cavity but the gas flow is such that any diffusion currents within the said cavity are significantly reduced and the fibers then deposit in the desired mat form.

The cover 3 for the receptacle 1 may be made of any high temperature resistant ceramic material such as alumina. Improved yields are obtained, however, using a ceramic cover made of a material which includes metallic oxides other than alumina, for example silica, zirconia, titania, iron oxide, chromium oxide, or cobalt oxide. The material of the cover may also contain a quantity (preferably between 1% and 10% by weight) of aluminum powder in combination with the ceramic material in the cover. The presence of the aluminum in the material of the cover will result in the formation of a more porous, or less dense, mat product. The cover may be made of a material which contains clay.

The receptacle may be made of material of the same composition as that of the cover. Preferably, however, the receptacle is made of ceramic material which contains between 1—20% by weight of finely-divided aluminum.

The manner of preparation of the cover and receptacle also is a factor in obtaining a good yield of fibers. Preferably the cover and receptacle are made by sintering powders at elevated temperatures, suitably in the range of about 2000°F. to 2500°F. This sintering procedure is particularly desirable when the ceramic material includes aluminum as a constituent.

The process of forming a mat article may be considered to take place in three stages, referred to herein as the pre-growth, growth and final growth stages.

No fibers grow during the pre-growth stage, but what takes place is reduction of surface tension of the aluminum charge in the ceramic receptacle. It is preferable, in the pre-growth stage, to use a very dry hydrogen gas stream maintained at a rapid flow rate. During the pre-growth stage of the process, the hydrogen gas should contain no more than 50 p.p.m. of water; and preferably not more than 20 p.p.m.

After the growth stage commences, however, the water content of the gas is increased substantially and the flow rate is reduced. Preferably the water content of the gas is increased incrementally throughout the growth period reaching a maximum in the final growth stage of the run. In the early stages of the growth stage, the water content of the gas is increased to about 300 p.p.m. and in the final growth stage, to 3000 p.p.m. Up to 40,000 p.p.m. of water may be used, however.

The pre-growth stage usually lasts about ten minutes or less. The dry hydrogen gas may generally flow at a rate of between about 0.01 and 0.06 cu. ft./sec., and optimally at about 0.03 cu. ft./sec. During the growth period, the hydrogen flow rate in the early stages of growth is preferably in the range of 0.001 to 0.003 cu. ft./sec. (0.001 cu. ft./sec. being considered more favourable). During the final stages of growth, a flow rate of 0.0001 cu. ft./sec. is preferred. These flow rates are relative to the dimensions of the apparatus used, which dimensions are described in detail in the Examples hereinafter.

The temperature of the melt may be held constant during the run, for example, between 2200°—3500°F. However, improved yields are obtained when the melt temperature is steadily increased during the growth and final growth stages, preferably from about 2500° to 3100°F., during a run of about an hour.

The yield of fibers can be enhanced if the receptacle is made of a suitable material. While alumina may be used, it is preferred to construct the receptacle of a fired intimate mixture comprising finely-divided particles of alumina and aluminum metal. The aluminum particles may amount to between 1 and 20% by weight of the material of the receptacle. Generally, the finer the particle size of the aluminum, the lower is the amount of aluminum required in the material of the receptacle. For example, at a particle size of 200 mesh, (i.e. particles small enough to pass through a mesh with apertures each 1/100 inch × 1/100 inch in size) an aluminum content of 2.5—7.5% by weight is preferred.

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

The receptacle is prepared by mixing finely-divided alumina, or an alumina composition, and aluminum powder, and firing at between 2000° and 2500°F., preferably at 2200°F., in air.

The charge consists of aluminum pellets

distributed evenly on the bottom of the receptacle. Alumina powder may be mixed with the pellets, in an amount between 5 and 50% by weight of the charge, if desired. The presence of this powder improves the yield of fibers.

FIGURE 2 illustrates the formation of a mat 4 comprising alpha-alumina single crystals fibers on the underside of the cover 3. While the mechanism of formation is not completely understood at present, it appears that deposition of said fibers occurs at spaced sites, indicated as 5, 6, 7. The fibers form and develop groups of fibers, each of which contains a plurality of individual fibers connected together substantially at a common point or site.

A typical single crystal alpha-alumina fiber has a ribbon or blade shape with a rhombohedral cross-section. Usually the fiber has a width-to-thickness ratio of between about 1:1 to 12:1, and a length from 10 to 25,000 times the width. Generally the length is from 0.5 to 4 inches, and the width is at least 0.5 micron. The effective diameters of the fibers generally are between about 1—30 microns.

As the fibers extend at least some of the fibers in each group become enmeshed with fibers of nearby groups. These enmeshings take place near a surface opposite to the cover surface, and thus the resultant mat article has one surface substantially covered with substantially separate enmeshed fibers.

FIGURE 3 illustrates separation of the cover 3 from the receptacle 1. A cluster of balls of alumina fibers 8 remains in the receptacle 1 as a by-product.

FIGURES 4 and 5 are side and top views, respectively, of the mat article 4, the fiber enmeshings nearer to one surface of the mat article being visible.

FIGURE 6 shows secondary growth fibers 10a, 10b, 10c, which occur nearer to one surface of the mat article during the run. The fibers 10a, 10b, etc. further increase the number of enmeshed fibers nearer to the surface of the mat article closest to the charge.

The bulk density of a typical mat generally is between 0.008 and 0.03 grams per cc. As described above, the density may be influenced by adjusting the distance of separation between the charge and the cover. Alternatively the density may be adjusted by varying the aluminum content of the cover.

The mat article of single crystal alpha-alumina fibers may find practical usefulness in various applications. In general these applications utilize the high strength or insulating properties of the fibers. For example, a thin fused laminate composite of a synthetic plastics material (for example an epoxy resin or a phenolic resin or a urethane resin) and the mat article has a high interlaminar shear strength as well as high fatigue strength. The combination of these properties is desirable when the laminate is used, for example, to make compressor blades where its low weight as compared to metals is advantageous. Other applications include centrifuges and body armour.

The mat article is useful as an additive to a ceramic to make a resultant composite of good toughness and tensile and impact strength. For example, sparking plug bodies of superior quality may be made by forming a slip of a ceramic powder and the alpha-alumina mat, and sintering the mixture.

Other applications of the mat article include use as a thermal insulation medium in the temperature range above the silica fiber range, e.g., to 3600°F.; in thermo-electric devices; as a filter medium, e.g., for hydrogen fluoride or chlorine trifluoride; as a substrate for deposition of electronic materials, particularly the epitaxial deposition of semiconductors; and as a support for spinning wool into a yarn or weaving into a cloth.

Porous composite structures may be formed with a metal, such as tungsten, nickel, cobalt or chromium, and the mat material. The resulting article is a low density structure with interconnecting porosity, which is suitable for engine or gas diffusion applications. The mat article may thus have plastics, ceramic or metal material incorporated in the spaces between the fabrics.

The following Examples further describe how the invention may be performed.

Example I

An alumina boat having the internal dimensions 5 inches wide × 17 inches long × 2 inches deep and weighing about 3 lbs. 4 oz. is charged with 8 oz. of aluminum pellets which are spread evenly on the bottom of the boat. An alumina cover having the dimensions 5 1/2 inches wide × 17 1/2 inches long × 1/2 inch thick is loosely positioned on the receptacle. The distance between the top of the charge and the underside of the cover is about 1/2 inch. The charged boat fitted with the cover is inserted into a furnace having a cross-sectional open area of about 20 square inches, thus leaving an effective open area of about 12 square inches. The temperature of the furnace is set at 2775°F. Purified hydrogen containing less than 20 p.p.m. of water vapor is admitted into the furnace to flow 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, whereupon 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. Mat formation begins on the underside of the cover. After 20 to 30 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 and cover are then removed from the furnace and cooled to room temperature. A relatively porous mat article is obtained, having a bulk density of about 0.008 grams per cc.

EXAMPLE II

A boat for the aluminum charge is prepared by mixing 3 lbs. 2 ozs. of alumina powder and 0.16 lbs. of 200 mesh (as hereinbefore defined) aluminum powder (5% by weight of aluminum) in a slip-casting mould. The ceramic is fired in air at 2200°F. for about a half-hour. A cover for the boat is prepared in a similar manner. The boat and cover are used in place of the alumina boat and cover in Example I for effecting a method otherwise similar to that of Example I.

EXAMPLE III

A boat for the aluminum charge is prepared by mixing 3 lbs. 2 ozs. of ceramic powder 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 lbs. of 200 mesh (as hereinbefore defined) aluminum powder (5% by weight of aluminum) in a slip-casting mould. The ceramic is fired in air at 2200°F. for about a half-hour. A cover for the boat is prepared from a similar ceramic composition. The boat is charged with 8 ozs. of aluminum pellets. A method similar to that of Example I is effected, and yield of fibers is excellent. The individual fibers have an effective diameter of between about 1—3 microns. Each fiber is about 1/16 to 1/2 inches in length. The dimensions of the mat article are about 3 3/4 inches wide × 16 inches long × 1/4 inch thick. The fibers are alpha-alumina single crystals of either rhombohedral or hexagonal cross-section, generally of rhombohedral cross-section. The bulk density of the mat article is 0.013 grams per cc.

EXAMPLE IV

A method as in Example III is effected, but with the use of a cover of material which contains 1—5% by weight of 200 mesh (as hereinbefore defined) aluminum powder added to the above composition. The result is a mat article which is substantially more porous, having a bulk density of 0.010 grams per cc., but with individual fibers having a larger diameter of between about 3—30 microns, generally about 10 microns.

EXAMPLE V

A cover is prepared from the following materials: 71% by weight alumina, 12% by weight clay, 12% by weight of above composition, and 5% by weight titania. The receptacle is the same as in Example III. A method otherwise as in Example I is effected, to yield a mat article of structure and fiber sizes similar to those of the article obtained in Example IV, but with bulk density of about 0.03 grams per cc.

EXAMPLE VI

Methods as in Examples I to V are repeated, with different separation distances between the tops of the aluminum charges and the undersides of the covers. Under conditions otherwise similar to those in the previous Examples, a separation distance of 1/4 inch produces denser mat articles, whereas a separation distance of about 3/4 inch produces looser mat articles.

In all the above Examples there is employed a method of growing a mat article comprising interconnected groups of single crystal alpha-alumina fibers, including the step of passing hydrogen and water vapor over a charge of molten aluminum in a ceramic receptacle provided with a loosely-fitting cover of ceramic material so that deposition of said fibers occurs at spaced apart sites on the underside of said cover thereby to form enmeshed groups of said fibers wherein the fibers in each of said groups are connected together substantially at and radiate from one of said sites.

Attention is directed to Patent No. (Application No. 7005/68), (Serial No. 1203343) wherein an alternative method of making single crystal fiber mat articles is disclosed.

WHAT WE CLAIM IS:—

1. A mat article comprising interconnected groups of single crystal alpha-alumina fibers, each of said groups including a plurality of said fibers connected together substantially at a common point and at least some of the fibers in each of said groups being enmeshed with the fibers in another or others of said groups to form said mat article with two opposed surfaces, the common points at which the fibers in the respective groups are connected together being spaced apart at one of said surfaces, and the other of said surfaces being substantially covered with substantially separate enmeshed fibers.

2. A mat article according to claim 1, comprising secondary growth fibers attached to said enmeshed fibers.

3. A mat article according to claim 1 or 2, having a plastics, ceramic or metal material incorporated in the spaces between said fibers.

4. A method of growing a mat article comprising interconnected groups of single crystal alpha-alumina fibers, including the step of passing hydrogen and water vapor over a charge of molten aluminum in a ceramic receptacle provided with a loosely-fitting cover of ceramic material so that deposition of said fibers occurs at spaced-apart sites on the underside of said cover thereby to form enmeshed groups of said fibers wherein the fibers in each of said groups are connected

together substantially at and radiate from one of said sites.

5. A method according to claim 4, characterized in that the distance of separation between the top of the aluminum melt and the underside of the cover is adjusted to produce a required density of the mat article, the said distance of separation being decreased to obtain a denser mat article or *vice versa*.

6. A method according to claim 4 or 5, characterized in that said cover is made of material which contains between 1 and 10% by weight of aluminum.

7. A method according to claim 6, characterized in that said cover is made of material which contains clay.

8. A method of growing a mat article substantially as described in any of the Examples hereinbefore.

9. A mat article according to claim 1 or 2 or 3, when made by a method according to any one of claims 4 to 8.

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1203342 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*

Fig.1.

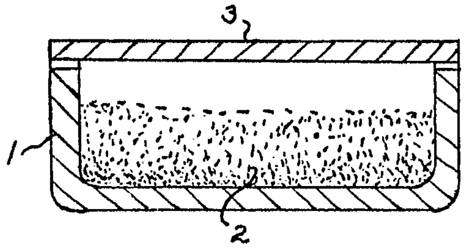

Fig.2.

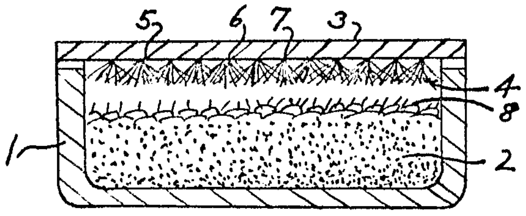

Fig.3.

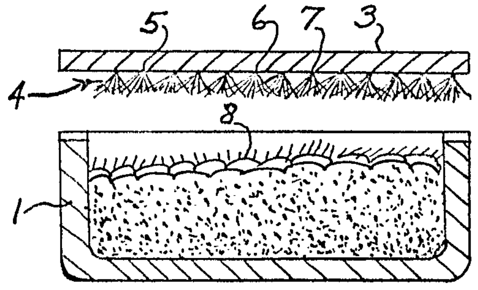

Fig.4.

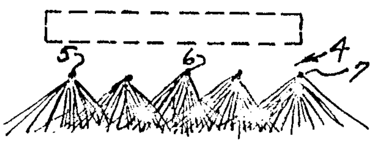

Fig.5.

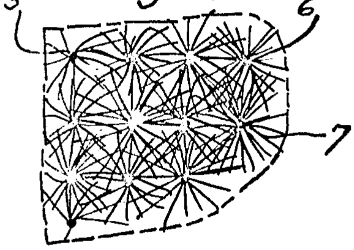

Fig. 6.