P-15 PAT. APPL.
IN-24
69484

NASA CASE NO. MFS-28431-1
PRINT FIG. #1

NOTICE

The invention disclosed in this document resulted from research in aeronautical and space activities performed under programs of the National Aeronautics and Space Administration. The invention is owned by NASA and is, therefore, available for licensing in accordance with the NASA Patent Licensing Regulation (14 Code of Federal Regulations 1245.2).

To encourage commercial utilization of NASA-owned inventions, it is NASA policy to grant licenses to commercial concerns. Although NASA encourages nonexclusive licensing to promote competition and achieve the widest possible utilization, NASA will consider the granting of a limited exclusive license, pursuant to the NASA Patent Licensing Regulations, when such a license will provide the necessary incentive to the licensee to achieve early practical application of the invention.

Address inquiries and all applications for license for this invention to NASA/Marshall Space Flight Center, Patent Counsel, Mail Code CC01, Marshall Space Flight Center, AL 35812. Approved NASA forms for application for nonexclusive or exclusive license are available from the above address.

Serial Number 07/812084
Filing Date December 23, 1991

(NASA-Case-MFS-28431-1) PRODUCTION OF MULLITE FIBERS Patent Application (NASA) 15 p
N92-17870
CSCL 11D
Unclas
G3/24 0069484

NASA CASE NO. MFS-28431-1

TECHNICAL ABSTRACT

PRODUCTION OF MULLITE FIBERS

A process for making mullite fibers wherein a hydrolizable silicon compound and an aluminum compound in the form of a difunctional aluminum chelate are hydrolized to form sols, using water and an alcohol with a catalytic amount of hydrochloric acid. The sols are mixed in a molar ratio of aluminum to silicon of 3 to 1 and, under polycondensation conditions, a fibrous gel is formed. From this gel the mullite fibers can be produced.

Inventor's Name:	Dennis S. Tucker J. Scott Sparks
Inventor's Employer:	NASA/MSFC
Serial Number:	07/812084
Filing Date:	December 23, 1991

Filing Date: December 23, 1991
Serial No.: 07/812084

PATENT APPLICATION
MFS-28431-1

Origin of the Invention

The invention described herein was made by an employee of the United States Government, and may be manufactured and used by or for Government purposes without the payment of any royalties thereon or therefor.

Background of the Invention

This invention in one of its aspects relates to the production of ceramics for aerospace use. In another of its aspects the invention pertains to mullite ceramics. In still another aspect the invention is directed to the production of mullite fibers, in particular to the production of continuous mullite fibers.

As aerospace technology rapidly moves forward, there is an ever increasing need for the development of materials capable of functioning at high temperatures without loss of structural integrity. As an example, fiber-reinforced ceramic-matrix composites have been identified as viable candidates for use in rocket engine applications, for instance in turbo-pump components. Multilayer insulation (thermal curtain) is used as a shield for vector-control devices in rocket boosters, and the search for more resilient materials is continuing. An object of this invention is the development of ceramic fibers which ultimately will find use in such applications. There are a number of ways to produce both continuous and discontinuous ceramic fibers. For example, melt spinning is widely used to produce glass and ceramic fibers. In melt spinning, materials are melted, then drawn through a spinnerette and wound onto a package. Typical examples of fibers produced by melt spinning are e-glass and s-glass. Less traditional compositions can also be formulated for melt spinning. In the American Ceramics Society Bulletin, for instance, in Vol. 68, No. 11, at page 1931 (1989) D. R. Messier describes the production of oxynitride glass fibers by the melt spinning method.

In Fiber Producer, Vol. 6, at page 55 (1983) R. J. Diefendorf describes chemical vapor deposition. In that process a solid is formed by deposition of decomposed or reduced gaseous molecules on a heated substrate. The method can also be used to form ceramic fibers. In the process, the substrate is a filament such as carbon or tungsten. Silicon carbide fibers are produced in this manner using carbon fiber as the substrate material.

Precursor polymeric fiber decomposition is another method used to produce ceramic fibers. The use of a polymeric precursor allows the fiber to be spun using, with appropriate modifications, procedures of the synthetic fiber industry. These spinning techniques include dry, wet, and air-gap wet spinning. Carbon, silicon carbide, alumina, and vitreous silica are examples of fibers which have been produced using such spinning techniques.

The invention herein is concerned with sol-gel ceramics. The production of glasses, ceramics and glass-ceramics, using the sol-gel method has received a great deal of attention in the past few years. In 1971 H. Dislich published his findings on sol-gel processing in Angewandte Chemie, International English Edition, Vol 10, page 363. Since that time, by the sol-gel process, researchers have been able to produce almost any type of multicomponent oxide using alkoxides of various metals. Applications include coatings, films, monolithic structures and fibers.

There have been a number of studies aimed at producing continuous and discontinuous fibers by the sol-gel method. In the American Society Bulletin, Vol 64, page 463 (1985), S. Sakka describes the sol-gel process and the production of silica-glass fibers by that synthesis. Herein it has been found that, under selected conditions, mullite fibers can be prepared using the process.

Summary of the Invention

The process herein is for the production of ceramics in the form of mullite fibers, suitable for use in fiber reinforced ceramic matrix compositions. To form the mullite fibers, the sol-gel process is used with modifications. A hydrolizable silicon compound, and an aluminum compound in the form of a difunctional aluminum chelate which undergoes hydrolysis, are both hydrolyzed to form sols. In hydrolyzing the silicon compound approximately twice as much water, approximately twice as much alcohol based on the silicon compound, and a catalytic amount of hydrochloric acid are utilized. In hydrolyzing the aluminum compound a quantity of water approximately equal to the amount of aluminum compound, approximately twice as much alcohol based on the aluminum chelate, and a catalytic amount of hydrochloric acid are employed. The sols resulting from these hydrolysis operations are mixed in a molar ratio of aluminum to silicon of 3 to 1, and under polycondensation conditions, including an elevated temperature, a fibrous gel is formed. From this gel the mullite fibers can be produced.

Detailed Description of the Invention

The production of glass and ceramics by the sol-gel method basically involves two steps: (1) hydrolysis to form a sol, along with polycondensation to form a preceramic gel; and (2) consolidation, or further polymerization to form the glass or ceramic structure. By the sol-gel process metal alkoxides are hydrolyzed with water using an acid catalyst in an alcohol solvent to form colloidal particles of the oxides. Water, alcohol, or both are then eliminated during the polycondensation reaction which forms the gel. The material is then heated at an appropriate temperature, usually a temperature in the range of 300 to 1500 degrees C. to produce either glass or ceramic depending upon the starting materials. Sakka and his co-workers produced glass fibers of TiO_2-SiO_2, Al_2O_3-SiO_2, ZrO_2-SiO_2, and Na_2O-ZrO_2-SiO_2. Polycrystalline ceramic oxide fibers such as ZrO_2, ThO_2, MgO, $ZrSiO_4$, TiO_2, Al_2O_3, $3Al_2O_3$-$2SiO_2$(mullite), and spin~~a~~el have also been produced by the sol-gel method. Attempts to prepare mullite fiber, and particularly continuous mullite fiber have not been successful. The production of mullite fibers is the object of this invention. It can, perhaps, best be understood by referring to the accompanying drawing.

DA? (12/14/91)
9SS (12/16/91)

In the drawing, Fig. 1 is a schematic showing the steps in the process.

In general the aluminosilicate sol-gel is prepared in a sealed reaction vessel under a blanket of nitrogen. The resulting gel is then poured into a spinnerette 2 supported by stand 4. The spinnerette is a stainless steel plate containing one hole. During spinning, dry nitrogen gas under a pressure of 35 to 50 psi is used to force the gel through the spinnerette hole. The extruded fiber 5 is then drawn around guide rollers 6 and 8 through coagulation bath 10. Desirably in that bath the fiber is treated by the procedure described by D. V. Varaprasad and A. S. Abbiraman in a Final Report to PPG Industries dated December, 1987, and entitled, "Sol-Gel Silica Fiber-Forming Operations." This coagulation bath is a mixture of deionized water and poly(ethyleneimide) (0.25 wt%). The pH of the coagulation bath 10 is adjusted using sodium hydroxide, the effects of pH and bath temperature having been tested using a matrix format.

From coagulation bath 10 the fiber 5 is pulled around roller 11 through a tube furnace 12, and onto a package 14. Laboratory motors (not shown) connected in series were used to control the winding speed. Using a 400μm spinnerette orifice, and a winding speed of approximately 30in/min (76cm/min) a fiber having a diameter of approximately 200μm could be continuously cured in the furnace for up to six hours.

To illustrate the invention in even greater detail the following specific examples of a preferred embodiment are given.

Example a Procedure

Tetraethoxysilane (TEOS), distilled water, HCl, and n-propanol were thoroughly mixed in a reaction vessel equipped with a thermometer, magnetic stirrer, condenser, heating mantle and thermowatch. The amounts of reactants used are given in the specific examples which follow. The reaction vessel was sealed so that the ingredients could be reacted under a nitrogen atmosphere to effect the hydrolysis of the TEOS. For the hydrolysis reaction the reaction vessel was heated to 40°C.

Under the same conditions aluminum diisopropoxide acetoacetic ester chelate (ADC), distilled water, HCl, and isopropanol were reacted to hydrolyze the ADC. Subsequently, in a ratio of ADC to TEOS of 3 to 1, the two sols resulting from the hydrolysis were combined and reacted, undergoing condensation polymerization to form a gel. The resulting aluminosilicate sol-gel was tested for spinnability, that is, to determine whether it would form fibers.

Example 1

Following the procedure of Example a, and using 14.8 grams (0.0708 mol) of TEOS, 0.4062 ml HCl, 26.7389 ml of isopropanol, and the quantities of water shown in Table 1, hydrolysis of the TEOS was effected. Similarly, using 57.2 grams (0.02088 mol) of ADC with 3.4230 ml of HCl and the 26.7389 ml of isopropanol the ADC was hydrolyzed. The molar ratios of the reactants were determined through a test matrix embodying twenty runs. In these runs, by varying the water in the range of 1.2 ml to 7.6 ml, the following ratios of ingredients were varied as shown in Table 1:

a = HOH/TEOS
b = HOH/ADC
c = HCl/TEOS
d = HCl/ADC
e = alc/TEOS+ADC
f = temperature
(+)=high
(-)=low
(0)=mean

Table 1

Run	a	b	c	d	e	f
1.	1.5(0)	1.5(0)	0.07	0.20	2.5	60(0)
2.	1 (-)	1 (-)	0.07	0.20	2.5	40(-)
3.	1 (-)	1 (-)	0.07	0.20	2.5	80(+)
4.	1 (-)	1 (-)	0.07	0.20	2.5	40(-)
5.	1 (-)	2 (+)	0.07	0.20	2.5	40(-)
6.	2 (+)	1 (-)	0.07	0.20	2.5	40(-)
7.	1.5(0)	1.5(0)	0.07	0.20	2.5	60(0)
8.	1 (-)	2 (+)	0.07	0.20	2.5	80(+)
9.	2 (+)	1 (-)	0.07	0.20	2.5	80(+)
10.	1 (-)	2 (+)	0.07	0.20	2.5	40(-)
11.	2 (+)	1 (-)	0.07	0.20	2.5	80(+)
12.	1 (-)	1 (-)	0.07	0.20	2.5	80(+)
13.	2 (+)	1 (-)	0.07	0.20	2.5	40(-)
14.	1.5(0)	1.5(0)	0.07	0.20	2.5	60(0)
15.	2 (+)	2 (+)	0.07	0.20	2.5	40(-)
16.	2 (+)	2 (+)	0.07	0.20	2.5	80(+)
17.	1 (-)	2 (+)	0.07	0.20	2.5	80(+)
18.	2 (+)	2 (+)	0.07	0.20	2.5	40(-)
19.	2 (+)	2 (+)	0.07	0.20	2.5	80(+)
20.	1.5(0)	1.5(0)	0.07	0.20	2.5	60(0)

In Runs 1 thru 20 the 3:1 molar ratio of ADC:TEOS compositions were heated to the temperatures shown in Table 1 for a period of 5 hours to overnight to promote the condensation polymerization to form the polymeric gel. Following gelation, the gel was considered spinnable at the point when a glass stirring rod could be immersed in the gel and a fiber could be drawn out of the resinous solution. Of the twenty runs in Table 1, only runs 6, 7, 9, 11, and 13 were spinnable. Those which could not be drawn gelled overnight forming a yellow product. Run 5, for example, resulted in an extremely yellow gel which was not spinnable. The spinnable gels, such as Run 6, while somewhat yellow, were more clear. The gel of Run 6 was spinnable after 5 1/2 hours. It could still be drawn after 47 hours. It appeared that the more clear the product became, the more readily it could be drawn.

It was learned that fibers could be produced by the process when the ingredients were within narrow ratios. In order of critically the silicon to aluminum alkoxide ratio was more important, then the alkoxide to water ratio, and next the alkoxide to catalyst (acid) ratio, and finally the alkoxide to alcohol ratio. Preferably, the TEOS, distilled water, hydrochloric acid, and isopropyl alcohol were thoroughly mixed in a 1:2:0.07:2.5 ratio, and the ADC, water, hydrochloric acid, and isopropanol were mixed in a 1:1:0.2:2.5 ratio. By the process of the invention, the premullite fibers can be continuously drawn as in the case of nylon, and continuous mullite fibers not available heretofore can be fabricated following the procedure described in conjunction with Fig. 1 of the drawings.

Example 2

To substantiate the reproducibility of the runs of Example 1, 14.8 gms TEOS, 2.5510 ml HCl, 1.2755 ml HOH, and 13.5 ml isopropyl alcohol were combined at 40°C. to hydrolyze the TEOS as set forth in Example a. In like manner 57.2 gms of ADC were mixed at 40°C. with 5.4250 ml HCl, 3.762 ml HOH, and 39.9 ml isopropanol. When hydrolyzed TEOS and ADC were mixed to form the gel the temperature rose to 56°C. The next day, approximately 23 hours later, the reaction product was more viscous, light green and spinnable. At about 48 hours at that low temperature the product had a viscosity approximating that of honey, and was very clear. When extruded by spinnerette and passed through the tube furnace at 500°C. the fibers had tensile strengths of 18,500 psi.

Mullite fibers can be produced herein whereas previous attempts were unsuccessful. Ultimately it will be possible to produce fibers useful in high temperature parts fabrications where many glass fibers are unsuitable. Heretofore the sol-gel process has been used for the production of spinels and non-fibrous mullite compositions. Hence, the invention herein provides a viable path to mullite fibers.

An important feature of this invention is the production of continuous mullite fibers by drawing the fibers through a tube furnace as shown in Fig. 1.

Having been given the teachings of this invention that the character of the alumina and silica sols, and hence the spinnability of the gels, is a function of the alcohol, catalyst, water ratios, ramifications will occur to those skilled in the art. Thus raw materials for the sol-gel process are well known. For instance in addition to tetraethoxysilane other silicon alkoxides or silanes can be used, for instance ~~trimethy~~l ~~methoxysilan~~e, di~~tri~~methyl 4SS 12/16/91 [illegible] 12/16/91
diethoxysilane, dimethyl dimethoxysilane, diethyl 4SS 12/16/91 [illegible] 12/16/91
dimethoxysilane, di~~tri~~methyl dipropionoxysilane and the like. 4SS 12/16/91 [illegible] 12/16/91

Since difunctional aluminum alkoxides gave improved results it is believed that some of the difunctionality carries over into the sol, leading to decreased crosslinking during polycondensation. Accordingly such aluminum alkoxides as the aluminum diisopropoxide acetoacetic ester chelate are preferred along with other difunctional aluminum alkoxides. ~~such as aluminum acetylacetonate, aluminum ethylenediamine tetra acetic acid, aluminum nitrilotriacetic acid, and others known in the art~~.

qSS 12/16/91
DD7 12/16/91

As another variation, reaction periods of minutes to days have been illustrated, indicating that some latitude is allowable in reaction temperatures upon which those reaction periods depend. Hydrolysis temperatures in the range of 40°C. to 100°C., and polycondensation temperatures in the range of 45°C. to 150°C.will normally be employed. These temperatures, as well as the furnace temperatures, are well known. Various forms of equipment will also occur to those in the field. Such modifications are, therefore, deemed to be within the scope of this invention.

PRODUCTION OF MULLITE FIBERS

Abstract of the Disclosure

Fiber-reinforced ceramic-matrix composites have been identified as viable candidates for use in rocket engine applications, for instance in turbo-pump components. Examples are glass and ceramic fibers such as carbon, silicon carbide, alumina, vitreous silica, e-glass and s-glass, as well as ceramic fibers formed on substrates such as carbon filaments, examples being silicon carbide fibers. A number of studies have been aimed at producing continuous and discontinuous fibers by the sol-gel method. Herein it has been found that, under selected condition, mullite fibers can be prepared using that process.

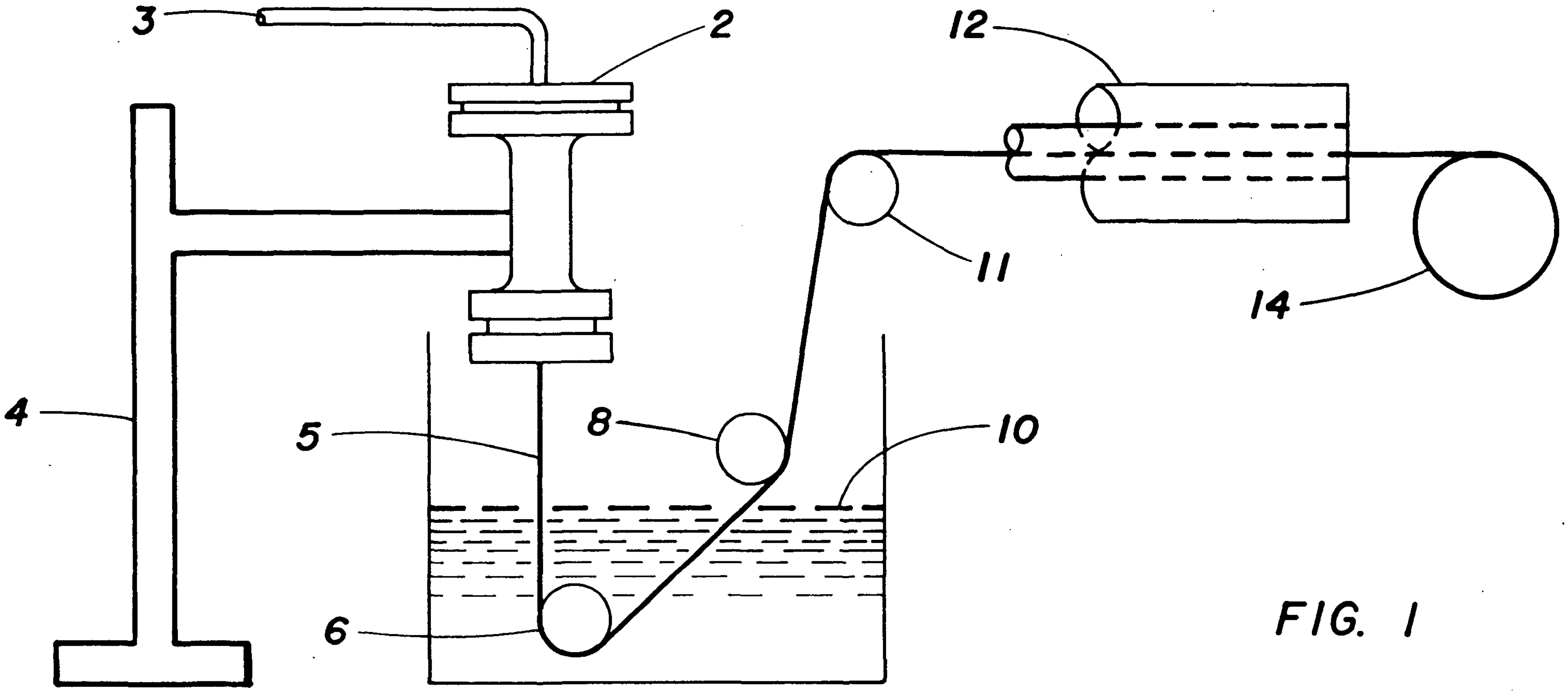

FIG. 1