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<b>(21) International Application Number:</b> PCT/US96/04366 <b>(22) International Filing Date:</b> 29 March 1996 (29.03.96)  <b>(30) Priority Data:</b> 08/414,369 31 March 1995 (31.03.95) US  <b>(71) Applicant:</b> HYPERION CATALYSIS INTERNATIONAL, INC. [US/US]; 38 Smith Place, Cambridge, MA 02138 (US).  <b>(72) Inventors:</b> MOY, David; 21 Edward Drive, Winchester, MA 01890 (US). NIU, Chun-Ming; 7 Sterling Street, Somerville, MA 01890 (US).  <b>(74) Agents:</b> EVANS, Barry et al.; Curtis, Morris & Safford, P.C., 530 Fifth Avenue, New York, NY 10036 (US).		<b>(81) Designated States:</b> AU, BR, CA, JP, KR, MX, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CARBIDE NANOFIBRILS AND METHOD OF MAKING SAME  <b>(57) Abstract</b>  A plurality of carbides, such as silicon carbide, tungsten carbide, etc., nanofibrils predominantly having diameters substantially less than about 100 nm and a method for making such carbide nanofibrils. The method includes the steps of: heating a plurality of carbon nanotubes or nanofibrils predominantly having diameters less than about 50 nm in a reaction chamber in the presence of a gas of the form $Q_nA_m$ , where Q is a metal capable of forming a carbide, A is an element or radical and n and m are integers necessary to satisfy valences, such as, for example silicon monoxide, and an inert gas in a reaction vessel to a temperature substantially less than 1700 C but sufficiently high to cause substantial reaction of the metal in the gas with the carbon of said carbon nanotubes or nanofibrils to form, <i>in situ</i> , solid carbide nanofibrils, the temperature being sufficiently low to prevent substantial fusing together of individual ones of said carbide nanofibrils, removing at least a portion of A-based gas from said reaction chamber as said reaction progresses, and maintaining said temperature until substantially all the carbon of said nanotubes or nanofibrils has been converted into Q-based carbide.		

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**CARBIDE NANOFIBRILS AND METHOD OF MAKING SAME****FIELD OF THE INVENTION**

The present invention relates to carbide nanofibrils and a method of making carbide nanofibrils.

5

**BACKGROUND OF THE INVENTION**

Ceramics are considered as the materials of the future. However, the ceramics are notoriously brittle. The many potential applications of ceramics as high temperature structural materials have been hindered by  
10 their lack of toughness and reliability.

In order to improve the toughness and reliability of ceramics, some efforts have been directed towards the development of nanophase ceramics and nanophase ceramic composites. Dramatically different  
15 properties can be obtained by making ceramic composites and by making ceramic materials into nanograin structured materials. For example, the toughness and strength of nanophase  $\text{Al}_2\text{O}_3$ -SiC composites are two to five times greater than those of the same materials with  
20 conventional structures, and a  $\text{Si}_3\text{N}_4$ -SiC nanophase composite can be stretched to two and a half times its original length at 1600°C.

Metallic carbide nanowhiskers, and in particular, silicon carbide (SiC) nanowhiskers (or  
25 nanofibrils) are of interest for their potential in the development of supertough ceramics matrix nanocomposites, and the preparation of metal matrix nanocomposites to improve the strength of metals. Potential applications of these nanowhiskers include nanophase carbides,  
30 nanophase ceramics, nanophase composites, and abrasive agents for high quality surface finish.

In order to achieve the desirable properties associates with SiC fibrils, or other metallic carbide fibrils, it is important that the fibrils have an  
35 extremely small, generally uniform diameter, substantially less than about 100nm. Heretofore,

however, it has not been possible to make SiC or other carbide fibrils in such extremely small dimensions.

SiC whiskers have been prepared by various methods, including hydrogen reduction of  $\text{CH}_3\text{-SiCl}_3$ , vapor transport of SiC, catalytic reaction of  $\text{SiO}_2$  and carbon in rice hulls, and vapor-liquid-solid techniques. However, most of the SiC whiskers produced by these methods have poorly crystallized polycrystalline structure. Their diameters are often bigger than 0.5 micrometer.

NASA Tech Briefs LEW-15415/16 describes deposition of SiC onto carbon tow of 5-10 micrometers (basically conventional PAN based fibers) by chemical vapor deposition, principally by use of  $\text{CH}_3\text{SiCl}_3$  and  $\text{H}_2$  as silicon deposition gas at a temperature of 1250 C. The resultant fibers had cracks and fissures, which were partially eliminated by incorporating the secondary pyrolytic carbon coating over the substrate. This document also includes a cursory account of an attempt to convert conventional carbon fibers (THORNEL M40) by using SiO gas at 1450 C for 30 minutes. An argon stream with 5-15% CO gas was used as a carrier gas to control the counter diffusion of SiO and CO gas. Moderate and widely varying strength (60-200 KSI) was achieved.

Zhou and Seraphin (Chemical Physics Letters 222 (May 13, 1994) 233-238, describe the preparation of single crystal SiC whiskers by direct reaction of carbon nanoclusters of DC arc generated nanotubes (i.e., clusters of buckytubes) retained on a carbon disc. The length and diameter of carbon nanotubes ranged from 1-5 micrometer and 20-40nm, respectively.

The disk containing the nanoclusters was placed on graphitic foil over SiO in a furnace and held at 1700 C, in a flowing argon atmosphere for two hours. The resulting SiC whiskers were about one order of magnitude longer and wider than the initial carbon nanotubes. The

SiC whiskers would also continue to grow if the reaction was allowed to proceed.

Although the starting carbon nanotubes had diameters in the range of 20-40 nm, the smallest SiC whisker shown had a diameter greater than 100nm. The lattice image of the whisker under TEM showed numerous defects.

It is believed that the resulting whiskers were frequently fused to one another at points of intersection. There are no distinguishing macrostructures or properties to relate the macroscopic morphology of the SiC fibers to the starting buckytube sample. Furthermore, the yield of SiC as fibers is low; only a small percentage of the carbon disc starting material (near the surface of the disc) was converted to SiC. Of the carbon material converted, a substantial amount is in the form of non-fibrous, amorphous particles or clumps.

Accordingly, although some attempts have been made to synthesize silicon carbide fibers and nanofibers, the prior efforts have not been successful in synthesizing high and consistent quality silicon carbide, or other carbide, nanofibrils predominantly in diameters substantially smaller than 100 nm.

#### **OBJECTS OF THE PRESENT INVENTION**

It is an object of the present invention to provide a plurality of metal carbide nanofibrils predominantly having diameters of less than about 100nm.

It is a further object of the present invention to provide such nanofibrils which are of high quality and generally unfused to one another.

It is a further object of the present invention to provide such metal carbide nanofibrils which are silicon carbide.

It is an object of the present invention to provide a method of making a plurality of carbide nanofibrils predominantly having diameters substantially

less than about 100nm, in situ, from carbon nanotubes or nanofibrils.

It is a further object of the present invention to provide a method of making such carbide nanofibrils  
5 from carbon nanotubes or nanofibrils which may be performed at relatively low temperatures.

It is a further object of the present invention to provide such a method for making silicon carbide nanofibrils.

10 It is further object of the present invention to provide an abrasive having a plurality of Q-based carbide nanofibrils predominantly having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.

15 It is a further object of the present invention to provide a nanophase high temperature, high strength composite material having a high temperature, high strength metallic base material reinforced with a plurality of Q-based carbide nanofibrils predominantly  
20 having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.

It is a further object of the present invention to provide a nanophase high temperature, high strength ceramic material having a plurality of Q-based carbide  
25 nanofibrils predominantly having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.

#### SUMMARY OF THE INVENTION

In accordance with a preferred embodiment of  
30 the present invention, a plurality of Q-based carbide nanofibrils predominantly having diameters substantially less than about 100 nm are provided, where Q is any metal capable of forming a carbide.

In accordance with another preferred embodiment  
35 of the present invention, a method of making a plurality of Q-based carbide nanofibrils predominantly having diameters substantially less than about 100 nm is

provided, comprising the steps of: heating a plurality of carbon nanotubes or nanofibrils predominantly having diameters less than about 50 nm in a reaction chamber in the presence of a Q-based gas of the form  $Q_nA_m$ , where A is an element or radical and n and m are integers necessary to satisfy valences, and an inert gas in a reaction vessel to satisfy valences, and an inert gas in a reaction vessel to a temperature substantially less than 1700 C but sufficiently high to cause substantial reaction of said Q-based gas with the carbon of said carbon nanotubes or nanofibrils to form, in situ, solid Q-based carbide nanofibrils and an A-based gas, said temperature being sufficiently low to prevent substantial fusing together of individual ones of said carbide nanofibrils, removing at least a portion of said A-based gas from said reaction chamber as said reaction progresses, and maintaining said temperature until substantially all the carbon of said nanotubes or nanofibrils has been converted into Q-based carbide.

In accordance with another preferred embodiment of the present invention, an abrasive is provided, comprising a plurality of Q-based carbide nanofibrils predominantly having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.

In accordance with another preferred embodiment of the present invention, a nanophase high temperature, high strength composite material is provided, comprising a high temperature, high strength metallic base material reinforced with a plurality of Q-based carbide nanofibrils predominantly having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.

In accordance with another preferred embodiment of the present invention, a nanophase high temperature, high strength ceramic material is provided, comprising a plurality of Q-based carbide nanofibrils predominantly

having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

These and other objects, features and advantages of the present invention will become clear to those skilled in the art upon review of the following description and figures, wherein:

Figure 1 is a schematic depiction of an illustrative reaction furnace for making carbide nanofibrils in accordance with a preferred embodiment of the present invention.

Figs. 2A is a TEM photomicrograph of a mass of SiC nanofibrils in accordance with a preferred embodiment of the present invention, converted from carbon nanotubes catalytically made from a carbon-based gas.

Figs. 2B is a SEM photomicrograph of SiC nanofibrils in accordance with a preferred embodiment of the present invention, converted from carbon nanotubes catalytically made from a carbon-based gas.

Fig. 3A is a TEM photomicrograph of a single crystal SiC nanofibrils converted from a buckytube, at a temperature of approximately 1200 C.

#### **DETAILED DESCRIPTION**

The present inventors have succeeded in producing a plurality of SiC fibrils predominantly having generally uniform diameters substantially less than 100 nm from a plurality of carbon nanofibrils or nanotubes having dimensions of about 50 nm or less by reaction with SiO gas at a relatively low temperature, sufficiently high to cause reaction of said Q-based gas with the carbon of said nanofibrils to form, in situ, solid SiC, but sufficiently low to prevent substantial fusing together of individual ones of said nanofibrils. This temperature is substantially less than 1700 C, and preferably in the range of about 1000 C to about 1400 C, most preferably approximately 1200 C.



The reaction appears to be a pseudo-topotactic transformation because the SiC nanofibrils produced inherited certain macroscopic morphological features of the starting carbon nanotubes or nanofibrils. The

5 resulting SiC nanofibrils appear to remain separate and predominantly unfused to other nanofibrils. The structure of individual nanofibrils appears to be single crystal Beta SiC. The diameters of the resulting SiC nanofibrils is about double that of the starting carbon

10 nanofibrils or nanotubes (~ 10-20 nm).

Example 1a. Carbon source

The carbon nanotubes used in this synthesis were BN ("bird's nest") and CC ("cotton candy") fibrils (Hyperion Catalysis). These carbon fibrils are produced by catalytic decomposition of carbon-based gas, such as hydrocarbon gas, and are characterized by substantially uniform diameters between about 7-12 nm, multiple graphitic carbon layers arranged concentrically around the tube axis, a hollow core and aspect ratios of about 10-500.

The foregoing nanotubes or nanofibrils are grown in aggregates having a macroscopic morphology of either bundles of relatively straight tubules or approximately spherical aggregates of highly intertwining, curved tubules resembling bird nests ("BN"), cotton candy ("CC"), or combinations of these. The individual tubules in any aggregate have a relatively narrow diameter distribution, the great majority being in the range of 7-9 nm for bundles, 8-12 nm for BN). In either aggregate morphology, essentially all the carbon is in the form of nanotubes. The inter-tubule distances in the aggregates are large, up to 100 nm (aggregates contain over 95% void volumes). These fibrils are generally free of a thermal carbon overcoat. Such fibrils and the manner of making them are described, for example, in U.S. Patent Application No. 08/532,400, filed December 8, 1994, U.S. Patent Application No. 149,573, filed January 28, 1988, U.S. Patent No. 4,663,230, and U.S. Patent No. 5,171,560, all of which are owned by the same assignee as the present invention. The contents of these applications and patents are incorporated herein by reference.

Although these starting carbon fibrils are preferred, other carbon nanotubes, such as carbon arc grown nanotubes and other carbon nanofibrils having diameters in the same general range, and up to about 50

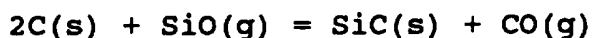
nm, may also be employed, although with generally less satisfactory results.

b. Procedure

Silicon monoxide (Johnson Matthey) was used as a silicon source. As showed in Fig. 1, the apparatus for the reaction consists of a tubular resistance furnace 10 comprising a quartz tube 15 with the end caps 20. 200 mg SiO 25 was placed in an alumina boat 30 and covered with quartz wool 35. 50 mg of carbon fibrils 40 were positioned on top of the quartz wool 35.

The furnace 10 was purged with argon through inlet tube 45 and out outlet tube 50 in the direction indicated by the arrows for 30 min., then heated up to 1200 C by means of heater 55. This temperature was maintained for 18 hours. The furnace 10 was then turned off, and cooled down to room temperature. The Ar flow rate during the reaction was: 60 cm<sup>3</sup>/min.

The chemical reaction can be formulated as:



In the furnace at the operating temperature, the SiO was vaporized into SiO gas and the SiO gas then reacted with carbon nanotubes to form SiC and CO. Subsequently, the CO gas was removed from the system by Ar carrier gas.

c. Results

After the reaction with SiO, the black color of the fibrils was changed to light greenish. The greenish color indicated the formation of SiC. Essentially the entire mass of starting carbon nanotubes was converted into SiC.

The macroscopic morphologies of the products were examined with SEM. SEM photos revealed that the products inherited certain morphological features of the starting carbon fibrils. The microscopic morphology of the products was characterized with TEM and select area electron diffraction.

As shown in Figs. 2A and 3A, the TEM photos revealed that the tubular carbon nanotubes have been

converted into solid SiC nanofibrils 60. The diameters of these nanofibrils are predominantly in the range of 10-20 nm and generally uniform for each of the nanofibrils (i.e., the diameter is generally uniform along the length of each shaft). Both X-ray and diffraction studies showed the SiC nanofibrils were crystallized with Beta SiC structure. Furthermore, the select area electron diffraction from single nanofibrils indicated that these nanofibrils are single crystal. However, polycrystalline forms are also expressly contemplated by the present invention.

Although the mechanism of reaction is not clear, it appears to be that the reaction of carbon nanotubes with SiO vapor is a pseudo-topotactic transformation because the process conserved the external structure, i.e., the kinky, somewhat intertwined macroscopic morphology of the carbon nanotubes. The typical diameters of the SiC nanowhiskers are about 20 nm, which are about twice the typical diameters of the starting carbon nanotubes. However, the SiC nanowhiskers may be as small as 5 nm.

From the Hyperion Catalysis carbon nanotubes, essentially only SiC nanofibrils with diameters ranging from 5-100 nm are obtained. Substantially all of carbon of the starting carbon nanotubes or nanofibrils is converted into SiC and substantially all of this is in the form of nanofibrils. The approximate distributions are:

	<u>Diameter, nm</u>	<u>%</u>
30	5-20	90
	20-50	9
	50-100	1

A few large diameter (< 100 nm) fibers with catalyst particles associated with them are also evident. However, these represent less than 1% of the total

product. Substantially all of the mass of SiC recovered is in the form of nanofibrils.

As can be seen in Figs. 2A and 2B, the SiC fibers are mostly present in aggregate form as kinky, somewhat intertwined individual fibers similar to the morphology of the carbon nanotubes which spawned them. The SiC fibers have slightly larger diameters than the starting carbon nanotubes, but not sufficiently larger to indicate growth by interfiber diffusion of SiC or by VLS. The similarity of the morphology of the individual SiC fibers to the initial carbon nanotubes indicates topotactic growth. Because the exact mechanism is not known with certainty, this is referred to herein as pseudo-topotactic.

## 15 Example 2

### a. Carbon source

A second example was conducted using a sample of buckytubes (core) purchased from MER Corp.

### b. Procedure

20 The procedure and temperatures were the same as described above in Example 1.

### c. Results

The distinguishing features of products from this example are: 1) even though there are some small diameter SiC nanofibrils present (one of which is shown in Fig. 3B as 65), these small nanofibrils represent a minor percentage of the total nanofibrils, and the diameter distribution is large, ranging from ~50 nm to several hundred nm; 2) there are no distinguishing macrostructures or properties to relate the morphology of the SiC fibers to the morphology of the starting buckytube sample; and 3) the yield of SiC as nanofibrils, as compared to the amount produced as other, non-fibrous shapes and structures is low.

35 The differences between the products described in the Zhou et al. article (using buckytubes at high temperature) and the present invention using either

buckytubes or nanotubes indicates that topotactic growth, characteristic of the present invention, occurs only at temperatures substantially lower than 1700 C (i.e., in the range of about 1000 to 1400 C vs 1700 C). At the  
5 higher temperature (i.e., approximately the 1700 C temperature of the Zhou et al. article), the fibers would be much thicker as a result of interfiber diffusion or sintering.

The generally uniform and very small size  
10 carbide nanofibrils in accordance with the present invention are useful for forming extremely fine abrasives, nanophase ceramics, nanophase ceramic composites, and as reinforcement in metal matrix nanocomposites using a high temperature, high strength  
15 metallic base material, particularly for high temperature, high strength applications such as gas turbine blades.

Other silicon source gases and combinations of gases may also be used besides the SiO source employed in  
20 the examples above. For example, a mixture of SiO<sub>2</sub> and Si at a temperature of 1000 C to about 1400 C may also be used. Other exemplary source gases include the following: SiH<sub>x</sub>Cl<sub>(4-x)</sub>, where x=integer; SiR<sub>x</sub>Y<sub>(4-x)</sub>, where x=integer, and R=alkyl, aryl, etc. Y=H or Cl;  
25 Si(ZR)<sub>x</sub>A<sub>(4-x)</sub>, where x=integer, A=R or Cl, R=alkyl, aryl, etc., and Z=O, N. Of course, these are only examples of silicon source gases and there is no intention of limiting the invention to these examples alone.

The pseudo-topotactic transformation of carbon  
30 nanofibrils to carbide nanofibrils in accordance with the present invention can also be accomplished with other metals which are capable of forming carbides. In this regard, boron, titanium, tantalum, niobium, zirconium, hafnium, molybdenum and tungsten, among others, are  
35 capable of forming carbides. The method of making carbides from these metals would be similar to the method for making SiC described in the example above, i.e., the

carbon fibrils are contacted with a gas based on the metal at a temperature substantially less than 1700C C, preferably between about 1000 C and 1400 C, and most preferably around 1200 C.

5                   Although the invention has been described herein in accordance with a preferred embodiment thereof, there is no intention of limiting the scope of the invention solely tot he preferred embodiment described. Rather, the scope of the invention is to be measured by  
10 the appended claims.

**We Claim:**

1. A plurality of Q-based carbide nanofibrils predominantly having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.  
5
2. The plurality of nanofibrils defined in claim 1, wherein said diameters are in the range of about 5-50 nm.
3. The plurality of nanofibrils defined in  
10 claim 2, wherein said diameters are in the range of about 5-20 nm.
4. The plurality of nanofibrils defined in claim 1,  
wherein most of the individual ones of said nanofibrils  
15 have a generally uniform diameter.
5. The plurality of nanofibrils defined in claim 1, wherein said nanofibrils are predominantly unfused to one another.
6. The plurality of nanofibrils defined in  
20 claim 1, wherein Q is silicon.
7. The plurality of nanofibrils defined in claim 6, wherein said nanofibrils are predominantly each a single crystal.
8. The plurality of nanofibrils defined in  
25 claim 7, wherein said single crystal has a Beta crystal structure.
9. The plurality of nanofibrils defined in claim 6, wherein said nanofibrils are polycrystalline.
10. A method of making a plurality of Q-based  
30 carbide nanofibrils predominantly having diameters substantially less than about 100 nm, comprising the steps of: heating a plurality of carbon nanotubes or nanofibrils predominantly having diameters less than about 50 nm in a reaction chamber in the presence of a Q-  
35 based gas of the form  $Q_nA_m$ , where A is an element or radical and n and m are integers necessary to satisfy valences, and an inert gas in a reaction vessel to a



temperature substantially less than 1700 C but sufficiently high to cause substantial reaction of said Q-based gas with the carbon of said carbon nanotubes or nanofibrils to form, in situ, solid Q-based carbide nanofibrils and an A-based gas, said temperature being sufficiently low to prevent substantial fusing together of individual ones of said carbide nanofibrils, removing at least a portion of said A-based gas from said reaction chamber as said reaction progresses, and maintaining said temperature until substantially all the carbon of said nanotubes or nanofibrils has been converted into Q-based carbide.

11. The method defined in claim 10, wherein said temperature is between about 1000 C and about 1400 C.

12. The method defined in claim 11, wherein said temperature is about 1200 C.

13. The method defined in claim 10, wherein the diameter of said carbide nanofibrils is no more than about double that of the carbon nanotubes or nanofibrils from which they were made.

14. The method defined in claim 10, wherein said carbide nanofibrils predominantly have diameters in the range of about 5-50 nm.

15. The method defined in claim 14, wherein said carbide nanofibrils predominantly have diameters in the range of about 5-20 nm.

16. The method defined in claim 10, wherein substantially the only source of carbon-containing material introduced into said reaction chamber is said carbon nanotubes or nanofibrils.

17. The method defined in claim 10, wherein Q is silicon.

18. The method defined in claim 17, wherein said A is oxygen.

19. The method defined in claim 17, wherein said carbide nanofibrils are predominantly each a single crystal.

20. The method defined in claim 19 wherein  
5 said single crystal has a Beta crystal structure.

21. The method defined in claim 17, wherein said carbide nanofibrils are polycrystalline.

22. The method defined in claim 10, wherein said carbon nanotubes or nanofibrils are of the type  
10 having multiple graphitic carbon layers arranged concentrically around the axis of each of said nanotubes or nanofibrils.

23. The method defined in claim 10, wherein said carbon nanotubes or nanofibrils are of the type  
15 generated by catalytic decomposition of a carbon-based gas.

24. The method defined in claim 10, wherein said carbon nanotubes or nanofibrils are substantially free of a thermal carbon overcoat.

20 25. A plurality of Q-based carbide nanofibrils pseudo-topotactically grown from a plurality of carbon nanotubes or nanofibrils having a macroscopic morphology, said carbide nanofibrils predominantly having diameters substantially less than about 100 nm, where Q is any  
25 metal capable of forming a carbide.

26. The plurality of Q-based carbide nanofibrils defined in claim 25, wherein said carbide nanofibrils are pseudotopotactically grown at between about 1000 C and 1400 C.

30 27. The plurality of Q-based carbide nanofibrils defined in claim 26, wherein said carbide nanofibrils are pseudotopotactically grown at about 1200 C.

28. The plurality of Q-based carbide  
35 nanofibrils defined in claim 25, wherein said plurality of carbon fibrils are made by catalytic decomposition of a carbon-based gas.

29. The plurality of Q-based carbide nanofibrils defined in claim 25, wherein said carbide nanofibrils substantially retain said macroscopic morphology of said plurality of carbon nanotubes or  
5 nanofibrils.

30. The plurality of carbide nanofibrils defined in claim 25, wherein said carbide nanofibrils predominantly have diameters in the range of about 5-50 nm.

10 31. The plurality of carbide nanofibrils defined in claim 30, wherein said wherein said carbide nanofibrils predominantly have diameters in the range of about 5-20 nm.

32. The plurality of carbide nanofibrils  
15 defined in claim 25, wherein most of individual ones of said nanofibrils have a generally uniform diameter.

33. The plurality of carbide nanofibrils defined in claim 25, wherein said nanofibrils are predominantly unfused to one another.

20 34. The plurality of carbide nanofibrils defined in claim 25, wherein Q is silicon.

35. The plurality of carbide nanofibrils defined in claim 34, wherein said nanofibrils are predominantly each a single crystal.

25 36. The plurality of carbide nanofibrils defined in claim 35, wherein said single crystal has a Beta crystal structure.

37. The plurality of carbide nanofibrils defined in claim 34, wherein said nanofibrils are  
30 polycrystalline.

38. An abrasive, comprising a plurality of Q-based carbide nanofibrils predominantly having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.

35 39. A nanophase high temperature, high strength composite material, comprising a high temperature, high strength metallic base material

reinforced with a plurality of Q-based carbide nanofibrils predominantly having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.

- 5                    40. A nanophase high temperature, high strength ceramic material sintered from a plurality of Q-based carbide nanofibrils predominantly having diameters substantially less than about 100 nm, where Q is any metal capable of forming a carbide.

## INTERNATIONAL SEARCH REPORT

 International application No.  
PCT/US96/04366

## A. CLASSIFICATION OF SUBJECT MATTER

 IPC(6) : D01F 9/08, 9/127, 9/12; C01B 31/30, 31/34, 31/36  
 US CL : 423/439, 440, 447.2; 428/367, 408; 51/307  
 According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 423/439, 440, 447.2; 428/367, 408; 51/307

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 4,663,230 (TENNET) 05 MAY 1987, col.4, line 47-7, line 16.	1-40
Y	Chemical Physics Letters, Volume 222, issued 13 May 1994, D. Zhou, et al., "Production of Silicon Carbide Whiskers from Carbon Nanoclusters", pages 233-238, especially page 237.	1-40
Y	US, A, 4,702,901 (SHALEK) 27 October 1987, col. 2, lines 16-69.	8, 20, 36
Y	US, A, 5,171,560 (TENNET) 15 December 1992, col. 10, line 51 - col. 12, line 2.	38-40

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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Date of mailing of the international search report

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