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PROCESS FOR PRODUCING METAL CARBIDE FIBERS, TEXTILES AND SHAPES

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8 Claims. (Cl. 23—344)

ABSTRACT OF THE DISCLOSURE

There is disclosed a process for producing metal carbide fibers, textiles, and shaped articles. The process involves the steps of:

(a) Impregnating a preformed organic polymeric material with a solution of a metal compound,

(b) Heating the impregnated material to evolve volatile decomposition products and to leave a carbonaceous relic containing the metal in finely dispersed form, and

(c) Further heating the relic to 1000°–2000° C. in a non-oxidizing atmosphere to form the metal carbide. Boron carbide and silicon carbide yarns produced by this process are attractive for high temperature structural applications.

This application is a continuation-in-part of Ser. No. 451,326 filed Apr. 27, 1965, Ser. No. 522,380, filed Jan. 24, 1966, Ser. No. 523,549, filed Jan. 28, 1966, and Ser. No. 576,840, filed Sept. 2, 1966, all by B. H. Hamling. The foregoing applications were all continuations-in-part of Ser. No. 320,843. Ser. Nos. 320,843; 451,326; 522,380 and 523,549 are now abandoned.

This invention relates to fibers, textiles, and shaped articles composed of metal carbides and to a process for producing such fibers, textiles, and shaped articles.

The prior art has prepared certain metal carbide fibers by a number of methods, but each is characterized by important limitations. For example, silicon carbide has been crystallized in a liquid system, but this procedure requires high pressures and/or high temperatures. In the "whisker" method, fibers are formed from the vapor phase or by electrolysis of molten salt. This method produces fibers which are often irregularly matted, kinked and very closely spaced. Moreover, metal carbide fibers made by the whisker method are characterized by distortions, and relatively short (below 0.25 inch). It has heretofore been impossible to reproduceably prepare flexible metal carbide fibers having a length-to-diameter ratio over 400, characterized by high strength at high temperatures.

On the other hand, it is widely recognized that such fibers would represent an approach to the upper limit for strength-to-weight ratio for a given material, due to the cohesive forces of adjacent atoms. It has been estimated that the weight of pressure vessels reinforced with high strength metal carbide fibers could be on the order of one-seventh that of conventional pressure vessels for high temperature uses.

Heretofore, also, there has been no completely satisfactory method for producing metal carbide articles of predetermined irregular or complicated shapes. Previous methods have involved machining or other shaping techniques, or in the case of foams, the use of various blowing agents. The methods were either difficult and complicated or were unable to provide close control over the final shape of the article.

It is an object of this invention to provide shaped metal carbide articles. Another object of the invention

is to provide a method for producing such articles from non-fibrous organic material. Still another object is to provide a variety of films, tubes, cups and other shapes which are composed of microcrystalline metal carbides.

It is also an object of this invention to provide an improved method for producing metal carbide fibers of small diameters of less than about 30 microns, which is reproduceable.

Another object is to provide such a method in which the metal carbide fibers are of uniform diameter, straight, smooth surfaced and free of distortions.

A further obpect is to provide metal carbide fibers of less than about 30 microns diameter having a length-to-diameter ratio over 400, which are flexible and characterized by high strength at high temperatures.

A still further object is to provide a variety of textile forms, including staple fibers, continuous tow and yarns, woven fabrics, batting and felts, composed of metal carbide fibers.

These and other objects and advantages of the present invention will be apparent from the following description and appended claims.

One aspect of the novel process comprises first providing a compound of a metal dissolved in a solvent, and immersing a preformed organic polymeric material in the resulting solution thereby swelling and opening the organic material interstices such that the metal compound is imbibed or absorbed in the interstices. The unimbibed metal compound is then removed from the organic material outer surfaces and the metal compound-imbibed material is dried. Next, the latter is first heated to temperature of at least 250° C. at a rate sufficiently low to evolve volatile decomposition products of the organic material without destroying the intergrity of this polymeric material. This pyrolysis step is continued for a sufficient duration to decompose the organic structure of the polymeric material and form a carbonaceous relic containing the metal in finely dispersed form. In the final carburization step, the relic is further heated from the pyrolysis step to temperature of about 1000–2000° C. in a non-oxidizing atmosphere to react the imbibed metal with the carbonaceous organic polymer relic to form a metal carbide shape, fiber, or textile. The non-oxidizing atmosphere of the carburization step may for example be that of an inert gas, hydrogen, or hydrocarbon reducing gas, vacuum or a combination of any of these atmospheres. There results a metal carbide shaped article which has essentially the same physical shape as the original preformed organic polymeric material, although the dimensions may be reduced by as much as about 40 to 60 percent.

Although I do not wish to be bound by same, the theory and mechanism of this process appears to be as follows: Microscopically, organic polymers such as rayon fiber are composed of extremely small crystallites of cellulosic chains (micelles or microfibrils) held together in a matrix of amorphous cellulose. The crystallites, approximately 40 Angstrom units (A.) in diameter and 250 A. long in high tenacity rayon yarns, are parallel to the axis of the rayon fiber and are spaced approximately 20 A. apart in the dry state. A one-denier fiber (1 gram weight per 9000 meters of length) has several million crystallites in its cross-section. When the fiber is immersed in a solvent such as water or aqueous solutions, it swells laterally opening the interstices, the amorphous regions enlarge and the crystallite spacing becomes approximately 50 A. (in the case of rayon). The dissolved selected metal compound such as a salt enters the swollen amorphous regions, which is about 85% of the volume of the swollen rayon, and becomes trapped in the amorphous regions between the crystallites when the solvent is evaporated from the fibers.

The metal compounds do not crystallize upon drying of the organic polymer, as would normally occur upon drying a solution, since they are effectively suspended and separated as islands about 50 A. in size between the crystallites.

The organic polymers may be imbibed with two or more metal compounds from the same solvent solution, so that carbides of more than one metal may be prepared, e.g. tungsten carbide and zirconium carbide. In the first approximation, most metal compounds enter the polymer interstices in direct proportion to their solution concentration, allowing ready control of the relative loadings of metal compounds in the preformed organic polymer. Due to the blocking action of the organic crystallites, the metal compounds cannot segregate from each other nor crystallize during the drying and heat conversion steps. Since they are finely dispersed, the metal compounds and later the oxides and carbides are extremely reactive and can be made to undergo the necessary chemical reactions to form the desired metal carbide alloy product at lower temperatures than normally required by conventional coprecipitation or powder blending methods for preparing such mixtures.

Any organic polymeric material can be employed as a starting material in the process of this invention providing it is characterized by the above-described sequence of extremely small crystallites held together in a matrix of amorphous regions which enlarge and admit the metal compounds on immersion in the solvent. Any class of materials which are composed of long-chain molecules held together by chemical cross-links may also be used. Any cellulosic material can be employed including rayon, cellophane, saponified cellulose acetate, cotton, wood and ramie. Other suitable organic materials include the protein fibers (wool and silk) and the man-made acrylics, polyesters, vinyls and polyurethanes. Certain organic materials such as polyethylene and polypropylene are not suitable for practicing the instant process because they cannot be swollen for imbibition of the metal compounds and/or the materials melt and lose their structure during pyrolysis. A preferred cellulosic material is rayon due to its structural uniformity, good imbibition characteristics and low impurity content.

The physical form of the elemental metal carbide composition is essentially the same as and is determined by the physical form of the organic polymer starting material. During conversion of the metal compound-imbibed organic fiber, for example, to the metal carbide fiber, the length of the fiber shrinks to approximately 40 to 60 percent and the diameter to 25 to 35 percent of the original dimensions. Similar shrinkage in all dimensions also occurs with the non-fibrous shapes. Where a yarn composed of a multiplicity of continuous-length metal carbide fibers is desired, a continuous-filament organic yarn is employed as the starting material in the process of this invention. Similarly, where a woven fabric or felt composed of metal carbide fibers is desired, a woven organic fiber cloth or felt can be used as the starting material. Of course, metal carbide woven textiles can be made using conventional textile equipment and techniques starting with metal carbide staple fibers or yarns made by the process of this invention.

In order to obtain adequate tensile strength in the final metal carbide fiber product, cellulosic materials are imbibed with the metal compounds to the extent of at least one-quarter mole and preferably 1.0–2.0 moles of the metal compound(s) in each "base mole" of cellulose. The term "base mole," as used herein refers to the molecular weight of a glycosidic unit of the cellulose chain (molecular weight of 162). With non-cellulosic materials, the degree of imbibition should be at least 0.1 and preferably 0.5–1.0 gram-equivalent metal ion in the metal compound imbibing solution per gram organic polymer. With lower concentrations of metal compound(s), insufficient metal salt is available in the relic to form a strong article and the process becomes less efficient in terms of metal carbide yield per unit weight of preformed organic polymer starting material. Another disadvantage of low metal compound concentrations is that more drastic oxidation conditions are necessary to achieve pyrolysis.

Imbibition or impregnation of the organic material can be carried out by several methods. Where the metal element which will appear in the final metal carbide fiber has salts which are highly soluble in water, the imbibition step can be carried out by immersing the organic material in a concentrated aqueous solution of such salt. For example, where a ZrC fiber is desired, the organic fiber can be imbibed by immersion in an aqueous solution of zirconyl chloride or zirconyl nitrate having concentrations in the range of 2.5 to 3.0 moles per liter. For salts which hydrolyze extensively (acid reaction) when dissolved in water, the acidity of the impregnating solution is preferably not greater than 1.0 molar (in hydrogen ion) in order to prevent degradation of the organic fiber during immersion. The acid may be neutralized with ammonia, if desired.

Pre-swelling the cellulosic organic polymers in water prior to immersion in concentrated imbibing solutions is preferably employed to increase both the rate and extent of salt imbibition. Water is also suitable for swelling protein materials. For acrylic and polyester polymers, aromatic alcohols are suitable swelling agents, and the ketones are useful in swelling vinyl and polyurethane polymers for the same purpose.

Water is the preferred solvent for metal compound-imbibing of cellulosic and protein materials such as wool and silk. Other solvents such as alcohols do not afford as efficient swelling of the polymers nor solubility of the selected metal compound for a high degree of imbibing. For vinyl and polyurethane polymers, esters and ketones are appropriate solvents, as for example normal butyl acetate or methyl ethyl ketone. For acrylic and polyester polymers, suitable solvents for the metal compound imbibition include aromatic alcohols and amines such as aniline, nitro-phenol, meta-cresol and paraphenylphenol.

Immersion times at normal temperatures (21–23 ° C.) required to give adequate imbibition vary from 30 minutes to several days depending on the salt(s) employed and the type of organic polymer employed. Immersion times greater than about 3 days in concentrated salt solutions are undesirable for fibers since the organic fiber may degrade, resulting in a decrease in amount of metal compound absorbed and causing the polymers to bond to each other. When it is desired to increase the rate of imbibition of the metal compound in the organic polymer to shorten the immersion time, the metal compound solution may be heated to as high as 100° C.

One method of impregnating rayon fibers and other cellulosic fibers and films with certain important metals is to absorb water into rayon and then contact the rayon with a compound of the metal so that it penetrates the fiber and hydrolyzes or reacts with the absorbed water to form insoluble metal oxide products. The metal oxide product remains in the fiber matrix without greatly disturbing the fibrous character of the rayon. The extent or amount of metal deposited within the fiber is directly a function of the amount of water absorbed in the rayon. Typical hydrolsis reactions are described by the following reactions:

$$SiCl_4+3H_2O\rightarrow H_2SiO_3+4HCl$$
$$TiCl_4+2H_2O\rightarrow TiO_2+4HCl$$
$$2BF_3+3H_2O \rightarrow B_2O_3 + 6HF$$
$$2TaCl_5+5H_2O\rightarrow Ta_2O_5+10HCl$$

The amount of water absorbed in the rayon fibers is readily controlled by exposing the fibers to air containing the desired amount of moisture. For maximum water absorption the rayon fibers may be immersed directly in liquid water. The amount of water absorbed in textile-

grade viscose rayon in equilibrium with moisture in air and liquid water at 75 ° F. is shown below:

Relative humidity at 75° F.:	Moisture content, percent of dry fiber weight
10	4
30	8
50	10
70	14
80	17
90	23
95	30
100 (immersed in water)	80–110

Some hydrolyzable metal compounds are liquid at normal conditions and the H_2O-laden rayon may be immersed directly in the metal compound to cause the hydrolysis product to be formed in the fiber. Examples of liquids are $SiCl_4$, $TiCl_4$, $VOC1_3$, $VC1_4$. However, many of the hydrolysis reactions proceed very rapidly with the evolution of heat. The resulting severe conditions may degrade or break up the fibers; in this event the metal compound is preferably diluted with a non-reactive, miscible liquid to avoid such conditions. Many non-polar organic liquids, such as benzene, toluene, hexane, carbon tetrachloride, chloroform, are suitable non-reactive liquids. These organic liquids, when used as diluents for the metal compounds, slow the rates of hydrolysis and help to dissipate the heat of reaction. Unreacted metal compound liquid (as well as any diluent) may be removed from between the fibers by evaporation, since they have high vapor pressures.

Other metal compounds which can be incorporated in fibers, films, and the like, by hydrolysis reaction but are not normally liquids are best utilized when dissolved in a non-reactive liquid, which is immiscible with water. Such metal compounds, for example, include $TaC1_5$, $NbC1_5$, $ZrC1_4$, $UC1_4$. Suitable solvents are bromoform, carbon tetrachloride, diethyl ether, and nitrobenzene.

Following imbibition with metal compound(s) from a solvent solution, it is necessary to remove excess solution from between the organic fibers before they dry in order to avoid bonding together of fibers by caked salt. Allowing excess unimbibed metal or hydrolysis product to remain on the fibers results in reduced strength and increased brittleness in the final metal carbide fiber product. For most cases, blotting thoroughly with absorbent paper or cloth using moderate pressure is sufficient for removing excess solution from the fibers. In addition, vacuum filtration and centrifugation have proven to be effective methods for removing excess solution from between the fibers. Raising the temperature of the wet fibers to 50–60 ° C. aids in removing excess solution from the fibers during blotting, vacuum filtration or centrifugation.

The metal compound-imbibed organic polymer is then thoroughly dried by any convenient means, such as air drying or heating in a stream of warm gas at a temperature not exceeding 70 ° C. It is desirable to dry the ploymer rapidly (in about one hour or less) to prevent expulsion of the metal compound from the interior of the organic polymer to its surface.

When a product containing two or more metal carbides is desired, the organic polymer is imbibed with compounds containing all of the desired metals. For example, if two or more water-soluble salts are employed, the imbibition can be carried out by a single immersion in an aqueous solution containing both salts. When two metals are desired, one of which is imbibed in organic polymers from aqueous solution and the second imbibed by hydrolysis of the metal halide or oxylhalide from organic solution, a preferred method is to imbibe first with the hydrolysis product and then with the water soluble salt.

In the next step of the process of this invention (decomposition of the organic polymer structure), the metal compound-imbibed organic polymer is heated under controlled conditions, namely: (1) to a temperature of at least 250 ° C., (2) at a rate sufficiently low to evolve volatile decomposition products of the polymer without destroying the polymer integrity, (3) for a sufficient duration to decompose the organic structure of said polymer and form a carbonaceous relic containing the metal compound in finely dispersed form.

It is necessary to heat the metal compound-imbibed polymer at a rate sufficiently low to avoid ignition of the polymer. If the organic polymer burns instead of carbonizes, the metal compound temperature rises execessively, due to its contiguous relation to the organic structure. Under such circumstances it is impossible to control the temperature, and the melting point of intermediate metal compounds formed may be exceeded or excessive crystallization and grain growth occurs. Also, the metal compound may be suspended in the organic compound vapors, and thus lost from the environment and unavailable to form the desired relic. Also, when ignition is avoided the product shaped articles, fibers, and textiles have smoother surfaces, are more free to bend, and are stronger. That is, very rapid heating and expulsion of the decomposition gases causes polymer continuity to be broken and results in excessive crystallization of the metal salt or oxide within the polymer relic which in the final analysis do not yield as smooth, flexible and strong metal carbide products as the unignited amorphous or poorly-crystalline, more dense intermediate metal oxide.

The first heating step is normally performed in a non-oxidizing inert atmosphere, as for example that provided by nitrogen, helium, argon, neon and the like, or a vacuum. However, if it is desirable to reduce the quantity of carbon remaining from the polymer pyrolysis step, a portion or all of this first heating step may be performed in an oxygen-containing atmosphere, perferably with between about 5 and about 25 volume percent oxidizing gas. The balance of the gaseous atmosphere comprises gasses which are chemically non-reactive with the environment, as for example the previously mentioned inert gases. In the event that an oxygen-containing gas is used, a portion of the carbon is removed as a carbon-containing gas through reaction with the oxidizing gas (volatilized). Oxidation provides a method for reducing the carbon content of the polymer relic, and controlling the molar ratio of carbon-to-metal for the ensuing carburization reaction. In general, pyrolysis of cellulose yields about four moles of carbon per mole cellulose as a residue, and the molar ratio of carbon to metal needed for a stoichimetric carburization reaction is between about 3/1 and 7/4.

The heating rate is affected by the environment whether inert or oxidizing, the latter being more difficult to control. In an oxidizing atmosphere the heating rate may be at least 100° C. per hour or higher, as long as polymer ignition is avoided. It is preferred to heat the polymer at a rate between 10° C. per hour and 100° C. per hour in an atmosphere containing from 5 to 25 volume percent oxygen, although higher heating rates may be satisfactory with effective means for venting the carbon-containing gas. Higher oxygen concentrations may be suitable, particularly during the later portion of the first heating step. The preferred oxidizing gas is oxygen, although other oxidizing gases such as nitrogen dioxide and sulphur trioxide can be used if desired.

When heating of the imbibed polymer is first begun (even in an oxidizing atmosphere), pyrolysis of the polymer to carbon is the predominant chemical reaction. The carbonized organic polymer comprises predominantly carbon but also can include small amounts of residual oxygen and hydrogen. If the heating continues and in an oxidizing atmosphere, oxidation of the carbon becomes the predominant reaction.

In the final process step of this invention, the relic from the first heating-pyrolysis step is further heated to a temperature between about 1000° C. and 2000° C. in a non-oxidizing atmosphere to react the metal with

the carbonaceous relic to form a metal carbide fiber, textile, or shaped article. the non-oxidizing atmosphere may be a vacuum, an inert gas as for example nitrogen, helium, or argon, or alternatively a reducing gas such as hydrogen or a hydrocarbon.

A carburization temperature of at least about 1000° C. is necessary to form a crystalline structure, which in turn provides a high-strength product. That is, the tensile strength of the metal carbide products of this invention is greater than 100,000 lbs. per square inch. It is desirable to limit the carburization temperature and time duration to achieve minimum grain size wihin the article. When producing fibers, crystal grain sizes of less than 0.2 of the fiber diameter are preferred. Larger crystal grain sizes reduce the fiber strength and flexibility. The rate of heating in the carburization step is not critical; rates of between about 200° C. per hour and 1000° C. per hour have been found suitable, although higher rates can be employed. Similarly the overall duration of the carburization step is not critical, and periods of between about 1 and 4 hours may be employed for a batch process, while much shorter times can be employed in a continuous process.

As previously indicated, any metal forming a stable carbide may be used to practice the invention. The preferred carburization conditions in terms of reaction temperature and molar ratios will of course very somewhat depending on the selected metal. It has been pointed out that in general the molar ratio of carbon to metal for a stoichiometric reaction is between about 3/1 and 7/4.

ous uses. For example they may be employed for reinforcing plastics for use at relatively low temperatures, and reinforcing metals and ceramics bodies at high temperatures, particularly where high strength, high Young's modulus, and low weight characteristics are desired. To reinforce plastics, the fibers should be either on and/or continuous within the geometrical shape of the structure because the loading to the embedded fibers is accomplished via a shear transfer process at the matrix-fiber interface. Since the shear strength of polymers is low, a greater transfer length (i.e., on fibers) is necessary if the fibers are to carry the major portion of the load. Short fiber-reinforced plastics generally show tensile strengths of about 50,000 p.s.i., whereas the same polymers reinforced with continuous fibers may exhibit strengths of 250,000 p.s.i. or greater. Boron carbide (B_4C) and silicon carbide (SiC) continuous filament yarns prepared by the present invention are particularly suitable for composite reinforcement.

Since these metal carbide fibers may be prepared in the form of cloth and continuous yarn, they may be used in filament winding of composite structures.

The metal carbide fibers, textiles, and shaped articles of the invention are generally useful in high temperature insulation, corrosion-resistant articles, and the like.

The process of the invention employs a "preformed" organic polymeric material. The term "preformed" means that the organic polymeric material has been fabricated into a fibrous or non-fibrous shape prior to impregnation with the metal compound.

TABLE I.—PREPARATION OF METAL CARBIDE FIBERS BY CARBURIZATION OF IMPREGNATED RAYON FIBERS

Metal carbide	Melting point, ° F.[1]	Preferred impregnation method	Carburization reactions	Carburization reaction temperatures, ° C.
TiC	5,685±160	$TiCl_3$ aqueous soln	$TiO2+3C \rightarrow TiC+2CO$	1,700–2,100
ZrC	5,750	$ZrOCl_2$ aqueous soln	$ZrO_2+3C \rightarrow ZrC+2CO$	1,800–2,200
HfC	7,030	$HfOCl_2$ aqueous soln	$HfO_2+3C \rightarrow HfC+2CO$	1,900–2,300
VC	5,160	VCl_3 aqueous soln. or hydrolysis of VCl_4.	$V_2O_3+5C \rightarrow 2VC+3CO$	1,100–1,200
NbC	6,330±230	Hydrolysis of $NbCl_5$ from ether solution.	$Nb_2O_3+5C \rightarrow 2NbC+3CO$	1,300–1,400
TaC	7,015	Hydrolysis of $TaCl_5$ from ether solution.	$Ta_2O_5+7C \rightarrow 2TaC+5CO$	1,300–1,500
Cr_3C_2	3,320–3,435	$CrCl_3$ aqueous soln	$3Cr_2O_3+13C \rightarrow 2Cr_3C_2+9CO$	1,400–1,800
Mo_2C	4,650	$(NH_4)_2MoO_4$ aqueous soln	$2MoO_2+5C \rightarrow Mo_2C+4CO$	1,000–1,400
MoC	4,875±90	do	$MoO_2+3C \rightarrow MoC+2CO$	1,000–1,400
W_2C	5,180±90	Ammonium tungstate aqueous solution.	$2WO_2+5C \rightarrow W_2C+4CO$	1,000–1,400
WC	5,200±90	do	$WO_2+3C \rightarrow WC+2CO$	1,000–1,400
UC	4,130–4,350	UO_2Cl_2 aqueous soln	$UO_2+3C \rightarrow UC+2CO$	1,200–2,000
UC_2	4,350	do	$UO_2+4C \rightarrow UC_2+2CO$	1,200–2,000
ThC	4,755±45	$ThCl_4$ aqueous soln	$ThO_2+3C \rightarrow ThC+2CO$	1,900–2,400
ThC_2	4,810±43	do	$ThO_2+4C \rightarrow ThC_2+3CO$	1,900–2,400
PuC		$PuOCl_2$ aqueous soln	$PuO_2+3C \rightarrow PuC+3CO$	1,200–2,000
PuC_2		do	$PuO_2+4C \rightarrow PuC_2+3CO$	1,200–2,000
B_4C	4,442	H_3BO_3 aqueous soln	$2B_2O_3+7C \rightarrow B_4C+6CO$	1,200–2,000
Al_4C_3	5,072	$AlCl_3$ aqueous soln	$2Al_2O_3+9C \rightarrow Al_4C_3+6CO$	1,400–1,900
SiC	4,900	Hydrolysis of $SiCl_4$	$SiO_2+3C \rightarrow SiC+2CO$	1,400–2,000

[1] From various literature sources.

It is preferred to effect carburization under about stoichiometric conditions when a substantially pure metal carbide product is desired. However, non-stoichiometric conditions can be used. For instance, excess carbon can be employed if the desired product is a metal carbide/carbon mixture.

One of the outstanding qualities of the present microcrystalline metal carbide products is their retention of flexibility and strength at high temperature. For this reason, the products are preferably formed using metals which form carbides having relatively high melting points of at least about 3300° F. On this basis preferred metals include those from Group IV–B (titanium, zirconium, hafnium), Group V–B (vanadium, niobium, and tantalum), and Group VI–B (chromium, molybdenum, and tungsten) of the Periodic Table, as well as boron, aluminum, silicon, thorium, uranium, and plutonium. Table I, below, lists preferred impregnation methods and carburization temperatures for the preparation of these metal carbides using rayon fibers.

The metal carbide fibers of this invention have numer-

The metal carbide shapes of this invention have a wide variety of uses. Metal carbide shapes prepared from organic foams or sponges are also useful as filters.

For use as filters it is preferred that the metal carbide shapes of this invention be prepared from cellulosic foams or sponges characterized by open porosity, uniform pore size and low density.

The metal carbide films of this invention are sheets which are highly uniform in thickness and which can be as 10 microns.

The following Examples 1–6 illustrate the process for preparing crystalline metal carbide products according to this invention.

Example 1.—UC fibers

7.1 grams of 1.5 denier regular viscose fibers were preswelled by immersion in water for one hour, and then immersed in 100 ml. or a uranyl chloride (UO_2Cl_2) aqueous solution having a molarity of 4.20 and a specific gravity of 2.11. Since the water in the preswollen region diluted the solution, the latter was replaced with a new

100 ml. of 4.2 molar UO_2Cl_2 solution. After ten minutes immersion in the solution, the fibers were removed and centrifuged to remove excess solution. The fibers contained 3.3 grams of solution per gram of rayon. They were dried in a warm air stream and after drying weighed 22.2 grams, including 1.57 grams imbided uranium per gram rayon. These fibers were next placed in a tube-type furnace and heated in a vacuum of about 1 micron Hg at a rate of 10° C./hour to 900° C. The furnace was then allowed to cool to room temperature under the vacuum. The resulting carbonaceous fiber relic weighed 14.9 grams and contained finely dispersed uranium with a carbon-to-uranium atom ratio of 3.7. The fibers were black lustrous and strong; there was no fiber breakage.

These carbonaceous fiber relics had approximately the correct carbon-to-uranium ratio for producing mono-uranium carbide fibers by heating to temperatures of about 1500–2000° C. in a nonoxidizing atmosphere. For example, UC fibers by the reaction $UO_2+3C \rightarrow UC+2CO$ can be prepared by heating uranium impregnated rayon fibers to about 1700° C. and maintaining this temperature level for a period of 1 hour in an argon atmosphere.

Example 2.—WC fiber cloth

The solution used for imbibing was made by dissolving 400 grams of ammonium paratungstate in 400 ml. of 30% hydrogen peroxide solution. The solution was heated to 60–70° C. at which temperature the ammonium paratungstate reacted with the hydrogen peroxide and dissolved in 5–10 minutes. The clear solution was then rapidly cooled to room temperature and contained 655 grams of tungsten per liter, with a specific gravity of 1.82 gms./cc. and a pH of 1.1. The rayon cloth was of 5 harness satin weave in both fill and warp directions using a textile grade viscose rayon yarn (1650 denier/720 filament), the cloth weight being 15 ounces per square yard. A 6 inch x 18 inch piece of cloth weighing 35.6 grams was immersed in the tungsten salt solution for 17 hours. The cloth was next centrifuged of excess solution and dried in warm air. The dried cloth contained 1.02 grams of tungsten salt/gram of rayon.

The cloth was converted to the tungsten carbide form by first heating in air at a rate of 20° C./hour to 300° C. and maintaining this temperature for four hours. The cloth was then further heated at a rate of 50° C./hour until 350° C. was reached and this temperature was maintained for four hours, thereby forming the carbonaceous fiber relic containing finely divided tungstein in dispersed form. The air in the tube furnace was then purged with nitrogen before the carburization reaction commenced. Dry hydrogen gas was passed through the furnace at a rate of 4 liters/minute (SPT) as the cloth was heated to 600° C. within 30 minutes and held at 600° C. for one hour, then heated to 1000° C. and held there for an hour. During the pyrolysis and carburization steps the cloth shrank from 6 inches x 18 inches to 3 inches x 10 inches. The weight of the tungsten carbide cloth was 73% of the weight of the starting rayon cloth.

The carburized cloth had the following physical and chemical characteristics:

(1) Appearance: Lustrous and metallic gray.

(2) Flexibility: Could be folded upon itself without creasing or breaking.

(3) Tear strength: 8 to 14 lbs./inch of width.

(4) Composition: By X-ray powder diffraction analysis, the cloth was composed chiefly of highly crystalline tungsten carbide (WC), (i.e. at least 80 wt. percent) and a trace of tungsten metal.

(5) Carbon content: 4.98 wt. percent.

(6) Specific gravity: 14.7 gms./cc. by the bromoform pycnometer method.

(7) Electrical resistance: 1.1 ohm per 1 inch width by 6 inches long (in the long dimension).

(8) Fiber diameter: 5–6 microns.

(9) Crystal grain size: 1 micron.

Example 3.—ZrC fibers

The starting rayon fibers were 1.5 denier viscose tow (133,000 continuous filaments in the tow). The tow weighing 6.8 grams was preswollen in water for 15 minutes prior to immersion in 2.84 molar $ZrOCl_2$ solution for four hours. It was next centrifuged of unimbibed solution from between the fibers and dried in air. The salt-loaded rayon tow weighed 12.5 grams and contained 0.84 gram zirconium salt per gram rayon.

The tow was placed in a tube furnace and heated under a vacuum of 1–10 microns Hg pressure at a rate of 50° C./hr. to 400° C. then 100° C./Hr. to 1000° C. The pyrolyzed fibers were black, had a high luster and weighed 6.0 gms. The fiber relics contained 33.7% carbon and 43.0% zirconium by weight.

In order to carry out the carburization reaction between the carbon and the zirconium the fiber relics were placed in a graphite crucible and heated at 1900° C. for two hours in a hydrogen atmosphere employing a high frequency induction furnace. The resulting fibers weighed 4.2 gms., had a black-gray color, showed no evidence of sintering together and had a diameter of 4–5 microns. They were very flexible and had a tensile strength between 100,000 and 150,000 p.s.i. The fibers were electrically conductive and X-ray powder diffraction patterns showed the fibers to be composed of polycrystalline face-centered-cubic zirconium carbide (ZrC). No graphite lines were evident in the X-ray patterns. The fibres were over 1 foot long with crystal grain size of less than 0.2 micron.

Example 4.—TiC fibers

A one-foot length of 9.0 denier viscose rayon tow (22,000 continuous filaments in the tow) was immersed in a 1.6 molar $TiCl_3$ aqueous solution for four hours. The tow was blotted of unimbibed solution and dried. The rayon tow containing the $TiCl_3$ salt was pyrolyzed and carburized in the same manner as described in Example 3. The product fibers were grayish-black, flexible, and had a diameter of 12–15 microns. The only crystalline phase present in the fibers as indicated by X-ray diffraction powder analysis was the face-centered-cubic titanium carbide (TiC). The crystal grain size was less than 0.5 micron and thus, less than 0.2 of the fiber diameter. Fibers of TiC having lengths of 50 feet have been prepared by the same method.

Example 5.—B_4C fibers

A one-foot length of 20 denier viscose rayon two (10,000 continuous filaments in the tow) was immersed in an aqueous solution containing 25% by weight boric acid for one hour. The solution was kept at 90° C. during the imbibment to keep the boric acid in solution. The two was then centrifuged while still hot to remove unimbibed boric acid from between the fibers. After drying the two in air it was subjected to the same pyrolysis and carburization treatment as described in Example 3.

The reacted fibers were black, free from each other, had appreciable flexibility and strength. X-ray diffraction analysis showed the fibers to be composed of crystalline boron carbide (B_4C). The fiber diameter was about 20 microns and the crystal grain size was less than 0.2 of such diameter.

Example 6.—SiC fibers

A length of 20 denier viscose rayon tow (10,000 continuous filaments in the tow) 23-inches long and weighing 13.3 grams was immersed in silicon tetrachloride liquid for 30 minutes. Prior to immersion, the two contained 1.4 gms. of absorbed water. After 30 minutes immersion reaction between the silicon tetrachloride and the water in the rayon was complete as indicated by the subsiding of HCl gas evolution from the fibers. The tow was freed of excess silicon tetrachloride by evaporation. The tow then weighed 15 gms. and contained 3.1 grams of silica. The silicon-loaded rayon two was pyrolized and car-

burized in the same manner as described in Example 3. The product fibers had a metallic luster, weighed 3.9 gms., and were characterized by appreciable flexibility and strength. X-ray diffraction pattern analysis indicated a mixture of crys'alline SiC and graphite. The fiber diameter was about 20 microns and the crystal grain size less than 0.5 micron.

Although preferred embodiments of this invention have been described in detail, it is contemplated that modifications of the process and composition may be made and that some features may be employed without others, all within the scope of the invention.

What is claimed is:

1. A process for producing crystalline metal carbide fibers, textiles, and shaped articles which comprises:

(a) providing a compound of a metal dissolved in a solvent;

(b) immersing a preformed organic polymeric material in the metal compound-containing solvent thereby swelling and opening the polymeric interstices such that the metal compound is imbibed in said interstices;

(c) removing the unimbibed metal compound from the outer surface of said polymeric material and drying the metal compound-imbibed polymer;

(d) first heating the metal compound-imbibed polymer to temperature of at least 250° C. at a rate sufficiently low to evolve volatile decomposition products of the polymer without destroying the polymer integrity, for a sufficient duration to decompose the organic structure of said polymer and form a carbonaceous relic containing the metal in finely dispersed form; and

(e) further heating the relic from first heating step (d) to a temperature in the range of about 1000°–2000° C. in a non-oxidizing atmosphere to react said metal with said carbonaceous relic to form a metal carbide article.

2. A process according to claim 1 in which said organic polymer is a fiber.

3. A process according to claim 2 in which said fiber is a cellulosic fiber.

4. Process of claim 3 wherein said cellulosic fiber is rayon.

5. A process according to claim 1 in which the first heating step (d) is at least partly performed in an oxygen-containing atmosphere at a rate sufficiently low to avoid polymer ignition and for a duration to evolve only a sufficient portion of the carbon from said organic polymer for adjustment of the metal/carbon stoichiometric ratio to that required to form the metal carbide article in further heating step (e).

6. A process according to claim 1 in which said metal is selected from the group consisting of Groups IV–B, V–B, and VI–B of the Periodic Table, boron, aluminum, silicon, thorium, uranium and plutonium.

7. A process according to claim 1 in which said metal compound is a salt which is converted to a metal oxide during the first heating step (d).

8. A process according to claim 1 in which the further heating step (e) is performed in a hydrogen atmosphere.

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