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COMPOSITE STRUCTURAL MATERIAL INCORPORATING METALLIC FILAMENTS IN A MATRIX, AND METHOD OF MANUFACTURE

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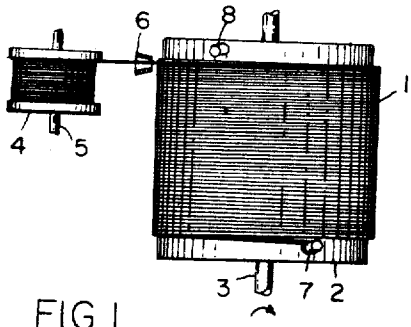


FIG. 1

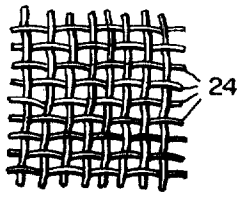


FIG. 3

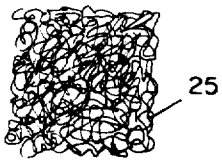


FIG. 4

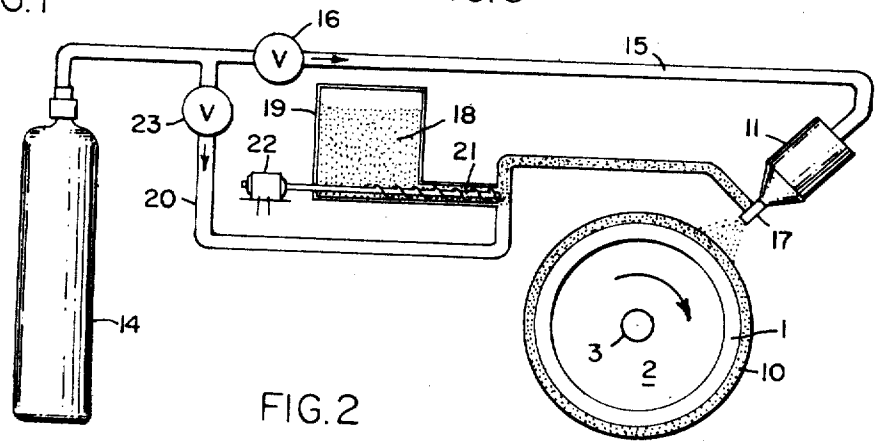


FIG. 2

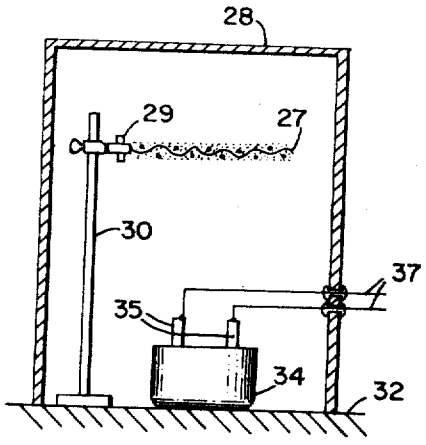


FIG. 5

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COMPOSITE STRUCTURAL MATERIAL INCORPORATING METALLIC FILAMENTS IN A MATRIX, AND METHOD OF MANUFACTURE

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Continuation-in-part of application Ser. No. 93,941, Mar. 7, 1961. This application Feb. 19, 1964, Ser. No. 346,388

U.S. Cl. 117—93.1 10 Claims

Int. Cl. C23c 7/00

ABSTRACT OF THE DISCLOSURE

A high strength composite structural material resistant to high temperature atmospheres consisting of high tensile strength metallic filaments within a high temperature resistant matrix. The matrix material has a melting point higher than the recrystallization temperature of the filamentary material and is deposited onto a mat of filamentary material by plasma arc spraying in an inert atmosphere. In order to maintain the high tensile strength of the filamentary material, the rate of deposition of the matrix is controlled so that the filamentary material is maintained below its recrystallization temperature.

This invention relates to composite structural materials, and more particularly to an improved composite structural material incorporating metallic filaments in a matrix, which is characterized by a high strength-to-weight ratio and resistance to deterioration in high-temperature atmosphere, and a novel method of manufacture thereof. The present application is a continuation-in-part of our copending application S.N. 93,941, filed Mar. 7, 1961, now abandoned.

In the development of composite structural materials, intensive efforts are being made to discover structures and combinations of materials which will afford improvement in such characteristics as specific strength, specific modulus, resistance to thermal shock, heat transfer rate, impact strength, erosion and corrosion resistance, and ease of fabrication. It has been found that fine elongated filaments of metallic materials exhibit extraordinarily high tensile strengths. For example, while the tensile strength of steel in ordinary structural forms may fall in a range below 100,000 p.s.i., a cold-drawn steel wire .004 inch in diameter may exhibit a tensile strength in the range of 500,000 p.s.i. Even greater tensile strengths are found in "whisker" crystals, which may be defined as single crystals having screw dislocations but very few edge dislocations. The tensile strength of whisker crystals may approximate the atomic cohesion strength of the metal; in the case of iron whiskers, strengths of 1,900,000 p.s.i. have been shown, and in the case of copper crystals, 430,000 p.s.i., each exceeding the tensile strength of large sections of the same metals by a factor of more than ten. The reason for this great strength is not clearly understood, but may be based upon the low incidence of edge dislocations which can exist within the small diameter of whiskers.

We have found that, by our improved method, fine metallic filamentary materials in the form of fine wires or whisker crystals may be embedded in a coalescent matrix of further material to form a composite material which exhibits improved characteristics. The tensile strength of the metallic filamentary material remains unimpaired by the process of encasing it in the matrix, so that an extremely favorable strength-to-weight ratio is obtained. The matrix material is deposited by a process which protects it from oxidation or other deleterious chemical action; and

the resulting composite shows exceptional resistance to erosion and cracking and high dimensional stability, when exposed to high temperature atmospheres. The composite material is therefore particularly useful in rocket nozzles and casings, and in other structures subjected to such atmospheres. The matrix material may be ceramic or metallic, and is preferably of a type having substantial resistance to erosion by chemical, thermal, or abrasive action.

The method of this invention permits utilization of desirable combinations of matrix and filamentary materials in which the melting point of the former is higher than the recrystallization temperature of the latter. In order to form a satisfactory structural material, it is necessary that the matrix material be caused to fully coalesce. However, if the matrix material is deposited en masse in a molten coalescing condition upon the filamentary material, and the recrystallization temperature of the latter is exceeded, the consequent grain growth of the filamentary material results in a substantial loss of the tensile strength of the filaments. The high strength characteristic which forms the principal advantage of such composite materials is thereby lost.

It is the primary object of the present invention to provide an improved method for forming a composite structural material having a high strength-to-weight ratio and resistance to deterioration in high temperature atmospheres. It is a further object to form an improved composite material from high tensile strength filaments and a coalescent matrix of a material whose melting point is higher than the recrystallization temperature of the filaments, without detracting from the tensile strength of the filaments. It is a further object of the invention to provide an improved method for forming a composite structural material through the practice of which improved physical characteristics may be achieved, particularly resistance to erosion and cracking, and dimensional stability when exposed to high temperature atmospheres. Further objects and advantages of the invention will become apparent as the following description proceeds.

Briefly stated, we carry out the method of our invention by first forming a plurality of fine elongated metallic filaments in a manner to develop a relatively high tensile strength therein, either by cold-drawing or by suitably heat-treating wire, or by utilizing whiskers in the as-formed condition. We then form a plurality of the filaments into a mat of any desired structural form. The filaments may have a random orientation or may be arranged in a systematic orientation, either in a parallel linear form, or in a woven or transversely oriented relationship.

We then select a matrix material having resistance to erosion by high temperature atmospheres, and a melting point higher than the recrystallization temperature of the filaments. This material is deposited in an inert atmosphere upon the mat of filaments in fine coalescing particles, at such a mass-rate that heat dissipation by the mat is sufficiently rapid to maintain the average temperature of the local area of deposition at a value less than the recrystallization temperature of the filaments. While the temperature in the immediate vicinity of impact of a particle may exceed the recrystallization temperature for a very brief interval, cooling occurs too rapidly to permit any deleterious grain modification to occur in the filaments.

Plasma-arc spraying techniques are preferably used, in which the matrix material is sprayed in fine particles, by a stream of inert gas such as nitrogen, through an electric arc which heats the particles at least to their melting point, and thence onto the mat. The particles coalesce upon the mat to form a dense solid matrix. The mass-rate of flow of the particles is held to a sufficiently small value to per-

mit the average temperature of the filaments in the local area of deposition to remain below their recrystallization point. To this end, the mat may be placed or wound upon a chill block to assist in the dissipation of heat therefrom. Alternatively, the matrix material may be vaporized and deposited upon the mat in the presence of a vacuum or an inert atmosphere, although this is a relatively slow method.

In some instances it may be desirable to subject the composite material to a slight reduction in thickness by a rolling operation subsequent to the formation of the matrix, for the compaction of the latter. The material may then be subjected to heat treatment to render the matrix more malleable, a a temperature below the recrystallization temperature of the mat material.

The composite structural material formed by our improved method exhibits a high strength to weight ratio corresponding to the original tensile strength of the filaments; and affords unitary structures having excellent specific strength and specific modulus, resistance to thermal shock, heat transfer rate, impact strength, erosion and crack resistance, and ease of fabrication. The matrix material serves not only to resist erosion, but also to bond the filaments for transmission of shear stresses therebetween. If desired, a number of layers of filamentary mats and matrix material may be formed in subsequent steps to afford a structure of increased thickness.

While the specification concludes with claims particularly pointing out the subject matter which we regard as our invention, it is believed that the invention will be more clearly understood from the following detailed description of preferred embodiments thereof, referring to the accompanying drawings, in which:

FIG. 1 is a view showing an illustrative method of winding a cylindrical mat of filamentary material in parallel orientation upon a mandrel;

FIG. 2 is a plan view of a woven mat of filaments;

FIG. 3 is a plan view of a mat of filaments having a random orientation;

FIG. 4 is a schematic view showing a first technique for depositing matrix material upon a filamentary mat; and

FIG. 5 is a schematic view illustrating a technique for applying matrix material to a filamentary mat by vapor deposition.

According to the invention, a selected material is first formed into filaments and treated to secure a high degree of tensile strength. For this purpose, cold-drawn or suitably heat-treated wire, or whisker crystals, may be utilized in the as-formed condition. The filamentary material is then formed into a mat of any desired configuration and filament orientation.

Referring to FIG. 1, there is shown an illustrative method for forming the mat. A cylindrical mat **1** of a selected continuous filamentary material, such as cold-drawn wire, is wound about a mandrel **2** rotatably supported on a shaft **3** of a conventional winding lathe (not shown). The filament is drawn from a supply reel **4** rotatably mounted upon a second shaft **5**, and is subjected to a suitable winding tension by friction means (not shown). A guiding thimble **6** moves axially of the mandrel, being fed by means (not shown) drivingly connected with the shaft **3** to wind the mat in closely laid helical convolutions as the shaft rotates in the direction shown by the arrow. The mandrel **2** need not be cylindrical in form, but may for example comprise a flat block to form a planar mat on either side thereof. The wire is initially secured upon a pin **7** fixed to the mandrel. Upon completion of the winding, the filament is broken and temporarily secured about a pin **8** fixed to the mandrel, or in any other suitable fashion.

Referring now to FIG. 2, preferred means are shown for depositing a matrix **10** upon the mat to form a composite structure in accordance with our improved method. These means include a plasma-arc spray gun **11** of a well-known type, in which an arc is generated between suitable electrodes (not shown) by an electric current supplied thereto by external electrical leads **12**. A stream of inert gas such as nitrogen is supplied to the gun from a tank **14** through a conduit **15** having a pressure regulating valve **16**, and issued at high velocity and high temperature from a spray nozzle **17** after passing through the aforementioned arc and being ionized therein. A supply **18** of a selected finely particulated matrix material is placed in a hopper **19** and is fed at a desired rate to the nozzle **16** by a suitable aspirator comprising a branch conduit **20** and a feed screw **21**. The feed screw is rotated at a preselected feed rate by a variable-speed motor **22** to feed the particles into the conduit, in which the particles are entrained by a flow of gas controlled by a pressure regulating valve **23**. The flow of matrix material is entrained in the stream of inert gas flowing from the nozzle, and is heated thereby to a coalescible condition. A stream of the particles impinges with the gas stream upon the surface of the mat **1**, coalescing thereon to form a rather dense matrix intimately bonded to the surface of the filament.

It may be found desirable to enclose the apparatus and the mat in a container and to establish an inert atmosphere therein, for preventing oxidation of the matrix material during the deposition step. Again, a jet of cool inert gas may be caused to impinge upon the mat surface at an angle to the stream of hot gas carrying the matrix particles, to minimize oxidation of the matrix material and to aid in cooling the mat surface by sweeping away hot gases. The presence of oxides in the matrix tends to detract from crack resistance.

The mass-flow rate of the particulated material to the mat is held to a sufficiently low value to permit the mat to dissipate heat from the coalescing particles rapidly enough to maintain the average temperature of the local area of deposition upon the mat below the recrystallization point of the filamentary material. The specific mass-flow rate varies widely and depends upon the size, melting point, and thermal capacity of the particles, the recrystallization point and thermal capacity of the filamentary material, and the rate of heat transfer to and heat dissipation from the mat and mandrel. However, an appropriate rate may readily be determined by experiment for a specific application, as will be apparent to those skilled in the art.

In order to assist in the rapid dissipation of heat, as well as to establish a uniform matrix thickness over the entire surface of the mat, the mandrel **2** is continually rotated on the shaft **3** during the deposition step. The mandrel additionally serves as a chill block for the removal of heat from the mat by conduction. In consequence of the local mode of deposition of the matrix, and the relatively low mass-flow rate of the matrix material onto the mat, the filamentary material is not recrystallized, but substantially maintains its initially high tensile strength. The resulting composite structure therefore exhibits very high strength characteristics. Following the deposition of the matrix, the pins **7** and **8** are removed from the mandrel and from the composite structure. If desired, additional matrix material may be deposited upon the internal surface of the structure, but the external application results in a matrix of substantial thickness being formed on the internal surface by penetration of the particles between adjacent windings.

Many alternative systematic orientations of the filamentary material in the mat may be used, and a woven arrangement of filaments **24** is shown in FIG. 3. Alternatively, the filaments may be randomly oriented as illustrated by the loosely intertwined fibers **25** shown in FIG. 4.

It will be apparent that a wide variety of structural forms may be produced by conforming a flexible mat of filamentary material to a mold of the desired configuration, and then depositing the matrix material upon the mat to produce a permanently formed composite struc-

ture. In some instances, it may be preferable to form the desired structural configuration from the finished composite material.

Referring now to FIG. 5, there is shown an alternative method of deposition of the matrix material. A planar woven mat **27** is shown supported by a clamp **29** upon a stand **30**, and is placed within a gas-tight container **31** upon a supporting surface **32**. The container is evacuated by any suitable means (not shown) to afford an inert atmosphere, or filled with a suitable inert gas such as nitrogen. A crucible **34** containing a supply of the selected matrix material is placed in the container, and a pair of electrodes **35** are inserted in the matrix material. An electrical current is supplied by means of leads **37** to the electrodes, of a value sufficient to heat the matrix material to the point of vaporization. The vapor condenses upon the lower surface of the mat **27** at a low mass-rate to form extremely fine particles, which coalesce thereon to form a rather dense and well-bonded matrix. This method deposits the encasing matrix at a relatively slow rate, however.

Following the deposition of the matrix upon the mat, cold rolling may be utilized if desired, to further compact the matrix for the elimination of any minute voids therein. Only a small reduction in thickness is required for this purpose. Following the cold-rolling operation, the material may be heat-treated according to conventional techniques at a temperature lower than the recrystallization point of the filamentary material, to improve the malleability of the matrix.

The following example is given to illustrate the advantages of a composite material prepared by our improved method. A filamentary mat of cold-drawn high-carbon steel wire having a diameter of .004 inch and an as-drawn tensile strength of 550,000 p.s.i. was prepared by winding the wire in parallel helical convolutions about a flat chill block. A matrix of aluminum particles having an average diameter of approximately 90 microns was deposited upon one exposed major surface of the mat by the plasma-arc spraying process to form a composite sheet having a total thickness of .006 inch. Additional layers of filamentary winding and matrix were applied to a total thickness of .035–.045 inch. The sheet of composite material formed upon one surface of the chill block was then removed by cutting the filament about the edges of the block, and cold-rolled to achieve a 5% reduction in thickness. The sheet was subjected to heat treatment at 500° F. for one-half hour to malleabilize the matrix. In this case, the filamentary material comprised 20% by volume of the composite sheet, which demonstrated a tensile strength, measured longitudinally of the wires, of 80,000 p.s.i. Another sheet was similarly prepared, but the steel wire comprised 36–38% of the volume of the composite structure; a tensile strength ranging between 160,000 and 200,000 p.s.i. was demonstrated, again measured longitudinally of the wires.

The composite material is useful in many applications, such as rocket nozzles and casings, for example, in which high strength-to-weight ratio, resistance to erosion and cracking, and dimensional stability in high temperature or erosive atmospheres, are of particular importance. A combination of tungsten wire matting with a tungsten matrix has been used to form a rocket nozzle throat and test-fired with highly satisfactory results. A throat having an initial diameter of 1.201 inches was fired for about 130 seconds at 5500° F., and showed a final diameter of 1.200 inches, the reduction being occasioned by a deposit of alumina from the propellant. There was no observable cracking or erosion after this firing.

The metals suitable for use as the filamentary material include, without being limited to, iron, molybdenum, tungsten, tantalum, chromium, nickel, beryllium, columbium, rhenium, boron, cobalt, titanium, aluminum, and vanadium and their alloys. Suitable matrix materials include, without being limited to, aluminum, titanium, magnesium, and their alloys, cermets and certain ceramics such as carbides, nitrides, borides, silicides, aluminides, oxides and forms of graphite. To illustrate the selection of appropriate combinations of filamentary material and matrix material, the following table is given for comparison of the recrystallization temperatures of a variety of suitable filamentary materials with the melting points of various matrix materials:

FILAMENTARY MATERIAL

	Minimum recrystallization temperature, deg. F. (approx.)
Iron or steel	900
Columbium	1500
Molybdenum	1700
Tungsten	2200
Tantalum	1900
Chromium	1100
Nickel	900
Titanium	1000

MATRIX MATERIAL

	Melting temperature, deg. F. (approx.)
Aluminum	1200
Titanium	3200
Magnesium	1160
Copper	1950
Tungsten carbide	5030
Titanium carbide	5660
Tantalum nitride	6050
Titanium boride	5250
Molybdenum disilicide	3680
Graphite	6870
Tungsten	6098

It will be understood that the foregoing list of materials is given purely for purposes of illustration, and it is not intended to limit the range of materials which may be selected in practicing the invention. The invention is particularly concerned with those combinations in which the melting point of the matrix material exceeds the recrystallization temperature of the filamentary material.

In the selection of whisker crystals as filamentary materials, it is to be noted that the ultimate tensile strength of all such materials is a relatively constant fraction of their respective moduli of elasticity. Therefore, the ratio of density to modulus of elasticity may be used as a convenient criterion for the choice of whisker materials to secure an optimum strength-to-weight ratio. Among suitable metallic whisker materials, the following exhibit particularly low ratios of density to modulus of elasticity (figures are in units of 10^{-9} inches): beryllium—1.5; chromium—5.8; molybdenum—7.1; vanadium—9.0; iron—9.8.

It will be apparent from the foregoing description that our improved method provides for the formation of composite structural materials having improved specific strength and specific modulus, resistance to thermal shock or other deterioration in high temperature atmospheres, heat transfer rate, impact strength, erosion and crack resistance, and ease of fabrication. In these structures, the filamentary material affords a high overall tensile strength, while the matrix material may, if desired, be selected to afford low overall density and improved resistance to erosion by chemical, thermal, or abrasive action. It will be apparent that by appropriate forming of a mat of filamentary material prior to the deposition of the matrix, rigid structures of any desired configuration may be prepared. Various changes and modifications will occur to those skilled in the art without departing from the true spirit and scope of the invention; we therefore intend to define the invention in the appended claims without limitation to specific illustrative embodiments herein described.

What we claim and desire to secure by Letters Patent of the United States is:

1. The method of forming a composite structural material characterized by a high strength-to-weight ratio and resistance to deterioration in high temperature atmospheres, which comprises the steps of: forming and treating fine elongated metallic filamentary material to obtain a crystal structure characterized by relatively high tensile strength which crystal structure tends to change to a crystal structure characterized by a lower tensile strength when said filamentary material is heated to the recrystallization temperature thereof; forming said filamentary material into a mat of a selected configuration; and encasing said mat in a substantially continuous coalescent matrix of a further material characterized by erosion resistance to high temperature atmospheres and having a melting point higher than the recrystallization temperature of said filamentary material, by depositing said further material by plasma arc spraying in an inert atmosphere upon said mat in fine coalescing particles at a mass-rate to maintain the average temperature of the area of deposition on said mat at a value less than the recrystallization temperature of said filamentary material.

2. The method of claim 1 wherein said matrix material is substantially free of oxides and is selected from the group consisting of metals, metal carbides, metal nitrides, metal borides, metal silicides and graphite.

3. The method of claim 2 wherein said filamentary material is tungsten and said matrix material is tungsten.

4. The method of forming a composite structural material characterized by a high strength-to-weight ratio and resistance to deterioration in high temperature atmospheres, which comprises the steps of: forming and treating fine elongated metallic filamentary material to obtain a crystal structure characterized by relatively high tensile strength which crystal structure tends to change to a crystal structure characterized by a lower tensile strength when said filamentary material is heated to the recrystallization temperature thereof; forming said filamentary material into a mat of a selected configuration; and encasing said mat in a substantially continuous coalescent matrix of metallic material having a melting point higher than the recrystallization temperature of said filamentary material, by depositing said matrix material by plasma arc spraying in an inert atmosphere upon said mat in fine coalescing particles at a mass-rate to maintain the average temperature of the area of deposition on said mat at a value less than the recrystallization temperature of said filamentary material.

5. The method of forming a composite structural material characterized by a high strength-to-weight ratio and resistance to deterioration in high temperature atmospheres, which comprises the steps of: forming a plurality of filamentary metal whisker crystals into a mat of a selected configuration, said whisker crystals being characterized by relatively high tensile strength which strength tends to decrease when said whisker crystals are heated

to the recrystallization temperature thereof; and encasing said mat in a substantially continuous coalescent matrix of material characterized by erosion resistance to high temperature atmospheres and having a melting point higher than the recrystallization temperature of said whisker crystals, by depositing said material by plasma arc spraying in an inert atmosphere upon said mat in fine coalescing particles at a mass-rate to maintain the average temperature of the area of deposition on said mat at a value less than the recrystallization temperature of said whisker crystals.

6. A composite structural material characterized by a high strength-to-weight ratio and resistance to deterioration in high temperature atmospheres produced by the process of claim 1.

7. A composite structural material characterized by a high strength-to-weight ratio and resistance to deterioration in high temperature atmospheres produced by the process of claim 2.

8. A composite structural material characterized by a high strength-to-weight ratio and resistance to deterioration in high temperature atmospheres produced by the process of claim 3.

9. A composite structural material characterized by a high strength-to-weight ratio and resistance to deterioration in high temperature atmospheres produced by the process of claim 4.

10. A composite structural material characterized by a high strength-to-weight ratio and resistance to deterioration in high temperature atmospheres produced by the process of claim 5.

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RALPH S. KENDALL, *Primary Examiner.*

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