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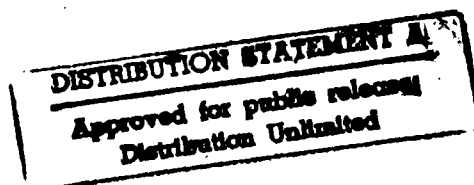
Inventor Paul M. Natishan
Arthur M. Morrish

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Docket No.: N.C. 72,578
Inventor's Name: Natishan et al,

PATENT APPLICATION

DIAMOND-REINFORCED MATRIX COMPOSITES

Background of The Invention

Field of the Invention

The present invention relates to composites, and more particularly to reinforced matrix composites.

Description of the Prior Art

In the past, diamond was either naturally produced or was grown in large high pressure/high temperature presses. The diamonds obtained from these processes consisted of single crystals of varying size. In recent years, advances in the production of synthetic diamond have changed dramatically the kind and number of materials applications for which diamond can be considered. Low temperature processes have been developed which produce diamond under a variety of pressure conditions ranging from less than 10 Torr to atmospheric. These techniques have the advantage of producing not only single crystal diamonds but also of directly depositing polycrystalline diamond films of a variety of thicknesses on virtually any properly prepared surface.

Diamond films, like bulk diamond, exhibit many desirable physical properties including excellent resistance to wear and

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Docket No.: N.C. 72,578
Inventor's Name: Natishan et al.

PATENT APPLICATION

1 chemical attack, a frictional coefficient near that of Teflon™, a
2 thermal conductivity five times that of copper, and high electrical
3 resistivity. It has also been demonstrated that these films have
4 the potential to improve the corrosion resistance of a metallic
5 substrate.

6 Composite materials have received much attention in the last 20
7 years because of their high specific strengths and stiffnesses.
8 Matrix materials have included polymers (organic matrix composites,
9 OMC), metals (MMC, inclusive of intermetallics, more specifically
10 abbreviated "IMC") and ceramics (CMC). Reinforced polymers and
11 ceramics are commonly used to make articles (both composite bulk
12 materials and composite coatings) having high strength and
13 stiffness. These articles can be used, for example, in dental
14 materials, cars, electronics, aerospace platforms, machinery and
15 sporting goods. Metal matrix composites have included, for
16 example, aluminum, copper, magnesium, tungsten, titanium, lead and
17 intermetallics such as TiAl. A considerable amount of research has
18 centered on the aluminum metal matrix composites, especially for
19 use in the aerospace and automotive industries. Magnesium MMCs
20 have also received much attention. The most widely used
21 reinforcement materials are (graphitic) carbon and SiC.

22 When metal matrix composites are fabricated or used at high
23 temperatures, reactions can occur at the matrix/ reinforcement
24 interface producing compounds that degrade the properties of the
25 composite including its strength, toughness and environmental

Docket No.: N.C. 72,578
Inventor's Name: Natishan et al.

PATENT APPLICATION

1 stability. Also, certain reinforcement materials can form galvanic
2 couples with some matrices. The presence of the galvanic couple
3 enhances the composite's susceptibility to environmental
4 degradation.

5 Further, there is a need for specialized composites having
6 high thermal conductivity, high electrical resistivity, and/or high
7 sound propagation velocity.

8
9 **Summary of the Invention**

10
11 It is an object of the present invention to provide metal,
12 polymer and ceramic matrix composites having long, useful
13 lifetimes.

14 It is another object of the present invention to provide a
15 metal matrix composite having an exceptional resistance to
16 corrosion.

17 It is a further object of the present invention to provide a
18 metal matrix composite free of galvanic couples.

19 It is still another object of the present invention to provide
20 composites with high thermal conductivity.

21 It is a yet further object of the present invention to provide
22 highly electrically insulating coatings on reinforcing materials
23 for composites.

24 It is still another object of the present invention to protect
25 reinforcing fibers from reaction with the environment, whether

aqueous or not, as well as with the matrix.

These and other objects are achieved by composites having diamond or diamond-coated inclusions. The inclusions may be particulates, platelets, or filaments (e.g., fibers, whiskers, or tubes). These composites combine the favorable structural properties of the matrix with the unique thermal, electrical, tribological, mechanical and acoustic properties of diamond. The chemical inertness and low electrical conductivity of diamond also prevents the formation of galvanic coupling between diamond or diamond-coated inclusions and metal matrices. The present invention is particularly useful when made as a lightweight composite.

Brief Description of the Drawings

A more complete appreciation of the invention will be readily obtained by reference to the following Description of the Preferred Embodiments and the accompanying drawings in which like numerals in different figures represent the same structures or elements, wherein:

Figs. 1(a) through 1(d) show several views of a diamond-coated SiC fiber produced by filament-assisted-chemical vapor deposition.

Fig. 2 is a Raman spectrum obtained from a coating deposited on a silicon carbide fiber and shows a peak at 1332 cm^{-1} , confirming

1 that the coating was diamond.

2 Figs. 3(a) and 3(b) show diamond coated tungsten fibers
3 produced by filament-assisted-chemical vapor deposition.

4 Fig. 4 is a Raman spectrum obtained from a coating deposited
5 on a tungsten fiber and shows a peak at 1332 cm^{-1} , confirming that
6 the coating was diamond.

7 Figs. 5(a) and 5(b) show diamond coatings on copper-coated
8 carbon fibers produced by filament-assisted-chemical vapor
9 deposition.

10 Figs. 6(a) and 6(b) are photomicrographs of a 20 vol.%
11 particulate DRC.

12
13 **Detailed Description of the Invention**
14

15 Any matrix material in is useful in a DRC according to the
16 present invention. Typically, these materials include polymers,
17 ceramics and metals. The metals may be, for example, aluminum,
18 copper, magnesium, titanium, lead, and alloys thereof, as well as
19 intermetallics. Preferably, the metal is aluminum or an alloy
20 thereof, especially where aluminum is the base metal, or magnesium
21 or an alloy thereof, especially where magnesium is the base metal.
22 Most preferably, the matrix metal is aluminum or an aluminum-based
23 alloy. Iron and titanium, Ti alloys or TiAl intermetallics are
24 less preferred as metal matrix composites because diamond may react
25 somewhat with these materials at useful temperatures.

1 The diamond or diamond-coated inclusions may be particulates,
2 platelets, whiskers or fibers, or a combination thereof. Each type
3 of inclusion geometry will have associated with it the known
4 benefits and disadvantages arising from its shape.

5 The inclusions can be consolidated with the matrix metal by
6 any of the standard composites techniques, and is present in a
7 volume percent sufficient to significantly enhance the thermal,
8 electrical, tribological, mechanical or acoustic properties of the
9 matrix. Generally, this amount corresponds to normal loading
10 fractions, typically about 10 to 50 volume percent. For example,
11 the DRC can have as little as about 0.1 volume percent, but
12 usually, at least 1 volume percent is included. Diamond or
13 diamond-coated inclusions oxidize at about 800°C, so processing
14 must be performed at temperatures below 800°C in an oxidizing
15 atmosphere, or in a non-oxidizing environment.

16 Diamond reinforcements may be natural crushed diamond, or
17 diamond made by any process. The dimensions of the reinforcements
18 will depend, in a known manner, upon the properties desired in the
19 final, reinforced product. Typically, particulates have about the
20 same dimensions in all directions and have average diameters of
21 about 10 nm to about 1 mm, typically about 1 μ m to about 50 μ m with
22 aggregates up to several hundred microns.

23 Diamond platelets are long in two dimensions and short in one
24 dimension. Typically, platelets have diameters of about 5 to about
25 200 μ m, preferably at least about 10 μ m.

1 Diamond and diamond-coated filaments (including fibers,
2 whiskers and tubes) are filamentous but may have other than the
3 standard cylindrical cross-section, such as star-shaped or
4 polygonal. Diamond-coated fibers are short in two dimensions and
5 essentially continuous in one dimension. Whiskers are short in two
6 dimensions, and of relatively small length. Diamond-coated
7 filaments may be made by a variety of different techniques. For
8 example, diamond-coated filaments can be made by coating substrate
9 filaments according to the process described by Morrish et al. in
10 U.S.S.N 07/516,585, filed April 30, 1990, the entirety of which is
11 incorporated herein by reference. For example, the surface of
12 substrate fibers may be scratched and coated with an oil prior to
13 depositing diamond thereon by chemical vapor deposition (CVD).
14 While preferable, scratching and oil-coating of substrate filaments
15 may not be absolutely necessary. For example, when the Morrish
16 process was used to produce a diamond coating on the molybdenum
17 substrate, diamond deposited on the untreated quartz filaments from
18 the reactor insulation. While quartz is not an ideal substrate for
19 diamond deposition, similar deposition should be possible upon
20 other, more preferable substrate filaments.

21 It has also been discovered that diamond filaments can be
22 produced by depositing diamond onto a filamentous substrate, such
23 as a graphite fiber, that can be removed by etching or other
24 suitable means after deposition has been completed. These diamond
25 filaments are also useful in the composites according to the

1 present invention. Additionally, if the substrate fiber is
2 extremely thin compared to the diamond coating thereon, the coated
3 fiber has the properties of a diamond fiber, and is essentially a
4 diamond fiber.

5 The method of depositing diamond on a substrate filament is
6 not particularly critical. Diamond can be deposited, for example,
7 by hot filament, microwave, dc plasma, oxyacetylene torch, etc.,
8 taking the known advantages and disadvantages of each technique
9 into account.

10
11 Having described the invention, the following examples are
12 given to illustrate specific applications of the invention
13 including the best mode now known to perform the invention. These
14 specific examples are not intended to limit the scope of the
15 invention described in this application.

16
17 **EXAMPLES**
18

19 **Example 1-The coating of fibers with diamond**

20 A variety of fibers have been coated with diamond including
21 silicon carbide (SiC), tungsten (W), copper (Cu), graphitic carbon
22 and copper-coated graphite (Cu-G). Fibers were scratched prior to
23 diamond deposition by placing them in a 0.25 micron diamond slurry
24 and sonicating for 30 minutes. The fibers were then oil coated and
25 placed in the deposition chamber.

1 Figs. 1(a) through 1(d) show several views of a diamond-coated
2 SiC fiber. Fig. 1(c) shows that the diamond coating is continuous.
3 This fiber was produced by filament-assisted-chemical vapor
4 deposition during a 6.5 hour growth using the following parameters:
5 the pressure was 40 Torr, the temperature was $825 \pm 25^{\circ}\text{C}$, the
6 filament temperature was $2,150 \pm 50^{\circ}\text{C}$, and the flow rate was 1
7 standard cubic centimeter per minute (SCCM) methane, and 100 SCCM
8 hydrogen. The thickness of the diamond coating was approximately
9 60 microns. The thickness of the diamond can be varied by changing
10 the deposition conditions. The Raman spectrum shown in Fig. 2, was
11 obtained from a coating deposited on a silicon carbide fiber and
12 shows a peak at 1332 cm^{-1} , confirming that the coating was diamond.

13 Figs. 3(a) and 3(b) show diamond-coated tungsten fibers.
14 These fibers were produced by filament-assisted-chemical vapor
15 deposition during a 4 hour growth using the following parameters:
16 the pressure was 40 Torr, the temperature was $825 \pm 25^{\circ}\text{C}$, the
17 filament temperature was $2,150 \pm 50^{\circ}\text{C}$, and the flow rate was 100
18 SCCM hydrogen and 1 SCCM methane. The Raman spectrum shown in Fig.
19 4 was obtained from a coating deposited on a tungsten fiber. This
20 spectrum shows a peak at 1332 cm^{-1} , confirming that the coating was
21 diamond.

22 Figs. 5(a) and 5(b) show diamond coatings on copper-coated
23 carbon fibers. These fibers were produced by
24 filament-assisted-chemical vapor deposition during a 4 hour growth
25 at a pressure of 40 Torr, the temperature was $825 \pm 25^{\circ}\text{C}$, the

Docket No.: N.C. 72,578
Inventor's Name: Natishan et al.

PATENT APPLICATION

1 filament temperature was $2,150 \pm 50^{\circ}\text{C}$, and the flow rate was 1 SCCM
2 methane and 100 SCCM hydrogen. As shown in those figures, bundled
3 fibers were simultaneously provided with a continuous diamond
4 coating lacking pinhole defects.

5
6 **Example 2-The fabrication of particulate DRCs**

7 DRCs were fabricated using standard powder metallurgy
8 techniques. The materials used to synthesize the DRCs were -230
9 mesh, 1100 aluminum powder and $30\text{ }\mu\text{m}$ diamond particles. The
10 quantities of matrix and reinforcement needed to produce the
11 desired volume fractions were determined and the required amounts
12 of powders were weighed on a laboratory scale. The powders were
13 mixed in a commercial vee blender. Blended powders were cold
14 isostatically pressed in latex tube molds at 100 ksi for 15 minutes
15 to form green compacts. Compacts were canned for hot isostatic
16 pressing (HIP) in stainless steel retorts and evacuated to a level
17 of $\sim 40\text{ mTorr}$. Samples were HIPped to full density at 600°C at
18 30 Ksi for 30 minutes. These processing conditions would have
19 dissolved regular carbon fibers and thus, show the greater
20 stability of diamond. Two sets of DRCs with volume fractions of
21 15% and 20% were produced. Figs. 6(a) and 6(b) show the 20 vol.%
22 particulate DRC and a lack of reaction products between the diamond
23 and the aluminum.

24 The elastic modulus of the DRC was 97.7 GPa, as determined
25 using the Piezoelectric Ultrasonic Composite Oscillator Technique

1 (PUCOT). Conservative estimates show that this value is 93% of the
2 rule of mixtures prediction. The modulus of 1100 aluminum is 70.3
3 GPa.

4 Electrochemical polarization testing in deaerated 0.1M NaCl
5 showed that the pitting potential of the 15 vol.% DRC was the same
6 as that of pure aluminum ($-0.700 V_{sce}$). It has been shown that the
7 pitting potential of a graphite - aluminum alloy MMCs was lower
8 (less positive) than that of the matrix material alone. A more
9 negative pitting potential indicates a decreased resistance to
10 pitting attack. It has been previously postulated that the lower
11 pitting potential was the result of reactions between graphite and
12 the matrix. The fact that the pitting potential of the DRC was the
13 same as that of aluminum may indicate that the reaction products
14 that resulted in a lower breakdown potential for the graphite MMC
15 did not form in the DRC. Anomalous pitting potential measurements
16 obtained on 1100 aluminum and 20 volume percent DRC, however, make
17 this conclusion uncertain.

18 Initial thermal conductivity measurements on the 15 vol.
19 percent DRC showed a decrease in thermal conductivity of the DRC
20 compared to that of Al. It is believed that this decrease is due
21 to the high Kapitza resistance between diamond and Al. If this
22 decrease arises from the high Kapitza resistance between diamond
23 and Al, then to take advantage of the high thermal conductivity of
24 diamond, the diamond must have be elongated (i.e., as a filament,
25 platelet, or large aspect ratio particle) in the direction of

1 desired heat transfer, or a loading fraction allowing inclusion to
2 inclusion contact through the material in the direction(s) of
3 desired heat transfer would need to be used. The possibility of
4 providing a material having directional thermal conductivity
5 provides exciting opportunities in the development of new thermal
6 management composites.

7
8 The novel materials of the present invention have several
9 unique and advantageous properties:

10 1) Since the thermal conductivity of diamond is five
11 times that of copper, DRCs can be used as thermal
12 management materials in electronic applications, computer
13 systems, optical components, or high heat flux structural
14 applications such as heat exchangers. Examples of matrix
15 materials include, but are not limited to, metals, such
16 as aluminum and copper, non-electrically conducting
17 polymers and ceramics. In the case where the high
18 electrical conductivity of a metal matrix cannot be
19 tolerated, an insulating diamond coating can be deposited
20 on the surface of the DRC. Such a coating also provides
21 more efficient heat collection. Finally, diamond-coated
22 fibers, diamond platelets, or diamond fibers can be
23 arrayed so that a DRC would have a locally varying
24 thermal conductivity, i.e. thermal conduits.

1 2) Since diamond has excellent resistance to chemical
2 attack, i.e. it is chemically inert, diamond or
3 diamond-coated inclusions inhibit reinforcement/matrix
4 reactions during fabrication or in applications at
5 elevated temperature. Also, since diamond is an
6 electrical insulator, galvanic couples between the
7 reinforcement and the matrix are avoided. The
8 combination of these two properties alone would lead to
9 a composite with greater stability, strength, and
10 durability. In addition, the hardness, the low
11 coefficient of friction, and the structural rigidity of
12 diamond are beneficial in producing composites with
13 improved and unique properties.

14
15 3) Properly prepared CVD diamond has a lower oxidation
16 rate than graphite at high temperature. Therefore, solid
17 diamond fibers, particles or platelets used as a
18 reinforcement material provide oxidation protection at
19 the reinforcement/matrix interface. In addition, a thin
20 coating of diamond on an otherwise susceptible
21 reinforcement material slows or prevents oxidation at the
22 fiber/matrix interface and preserves the properties and
23 integrity of these interfaces which are crucial to the
24 functioning of the composites.

1 4) Anti-oxidation coatings such as refractory oxides or
2 other protective coatings applied to carbon fibers and
3 other reinforcement materials often suffer from cracking,
4 spalling, and other failures due to the mismatch in the
5 coefficients of thermal expansion (CTE). By coating the
6 reinforcement with diamond prior to the final
7 anti-oxidant coating, the CTE mismatch gradient can be
8 minimized, and the bonding between the coatings and
9 reinforcement can be maximized, thereby improving the
10 durability of the coating and extending the usable
11 temperature range of the reinforcements.

12
13 5) The acoustic properties of diamond may be beneficial
14 in certain DRC applications because of diamond's high
15 sound propagation velocity, high stiffness, low weight
16 and low acoustic attenuation rate.

17
18 6) The diamond and diamond-coated inclusions, particularly
19 fibers, of the present invention could also replace
20 reinforcements such as fiberglass in matrices other than
21 metals. For example, diamond or diamond-coated inclusions,
22 especially fibers, may reinforce epoxy resin circuit boards,
23 providing them with the high thermal conductivity and strength
24 needed to support a high circuit density while maintaining
25 electrical resistance. Also, diamond or diamond-coated

Docket No.: N.C. 72,578
Inventor's Name: Natishan et al.

PATENT APPLICATION

reinforcements, especially fibers, can enhance the strength
and thermal conductivity of ceramic materials.

7) Diamond reinforced composites are attractive
materials for use in sporting goods, such as tennis
rackets, and other consumer products because of the
esoteric appeal of diamond, as well as diamond's unique
and advantages properties.

Obviously, many modifications and variations of the present
invention are possible in light of the above teachings.

Docket No.: N.C. 72,578
Inventor's Name: Natishan et al.

PATENT APPLICATION

ABSTRACT

A matrix composite includes diamond or diamond-coated inclusions. The inclusions may be particulates, platelets, whiskers or fibers. The matrix material may be, for example, a metal, a ceramic, or a polymer. These matrix composites combine the favorable structural properties of the matrix material with the unique thermal, electrical, tribological, mechanical and acoustic properties of diamond. The chemical inertness of diamond also prevents the formation of galvanic coupling between diamond or diamond-coated inclusions and metal matrices. The present invention is particularly useful when made as a lightweight composite. Typical metal matrix materials include aluminum, copper, magnesium, titanium, lead, and alloys thereof. When the composites include diamond-coated reinforcing inclusions, the coated substrate of the inclusion may be, for example, silicon carbide, tungsten, copper, graphitic carbon, or copper-coated graphite. The substrates of the inclusions may be coated with diamond, for example, by CVD.