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

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

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

When metal matrix composites are fabricated or used at high temperatures, reactions can occur at the matrix/ reinforcement interface producing compounds that degrade the properties of the composite including its strength, toughness and environmental stability. Also, certain reinforcement materials can form galvanic couples with some matrices. The presence of the galvanic couple enhances the composite's susceptibility to environmental degradation.

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

Summary of the Invention

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

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

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

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

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

It is still another object of the present invention to protect 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 that the coating was diamond.

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

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

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

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

Detailed Description of the Invention

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

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

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

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

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

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

It has also been discovered that diamond filaments can be produced by depositing diamond onto a filamentous substrate, such as a graphite fiber, that can be removed by etching or other suitable means after deposition has been completed. These diamond filaments are also useful in the composites according to the present invention. Additionally, if the substrate fiber is extremely thin compared to the diamond coating thereon, the coated fiber has the properties of a diamond fiber, and is essentially a diamond fiber.

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

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

EXAMPLES

Example 1-The coating of fibers with diamond

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

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

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

Figs. 5(a) and 5(b) show diamond coatings on copper-coated carbon fibers. These fibers were produced by filament-assisted-chemical vapor deposition during a 4 hour growth at a pressure of 40 Torr, the temperature was 825 ± 25°C, the filament temperature was 2,150 ± 50°C, and the flow rate was 1 SCCM methane and 100 SCCM hydrogen. As shown in those figures, bundled fibers were simultaneously provided with a continuous diamond coating lacking pinhole defects.

Example 2-The fabrication of particulate DRCs

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

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

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

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

Initial thermal conductivity measurements on the 15 vol. percent DRC showed a decrease in thermal conductivity of the DRC compared to that of Al. It is believed that this decrease is due to the high Kapitza resistance between diamond and Al. If this decrease arises from the high Kapitza resistance between diamond and Al, then to take advantage of the high thermal conductivity of diamond, the diamond must have be elongated (i.e., as a filament, platelet, or large aspect ratio particle) in the direction of desired heat transfer, or a loading fraction allowing inclusion to inclusion contact through the material in the direction(s) of desired heat transfer would need to be used. The possibility of providing a material having directional thermal conductivity provides exciting opportunities in the development of new thermal management composites.

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

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

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

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

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

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

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

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.

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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.