

PERFORMANCE ENHANCED HEAT SPREADER

5 BACKGROUND

The present invention relates to methods of applying a coating to a substrate of pyrolytic graphite and the coated pyrolytic graphite which exhibits an improved thermal conductivity. The coated pyrolytic graphite can be used as a heat spreader for conducting heat from a device. Electronic components are becoming smaller
10 while heat dissipation requirements are becoming greater. In order to dissipate heat generated by these electronic components, heat spreaders are utilized between the electronic component and a heat sink. Heat spreaders can be made of a solid thermally conductive metal. The solid conductive metal has a limited ability to spread heat and has limited thermal conductivity characteristics.

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INCORPORATION BY REFERENCE

All publications, patents, and patent applications mentioned in this specification are herein incorporated by reference to the same extent as if each
20 individual publication, patent, or patent application was specifically and individually indicated to be incorporated by reference, and as if each said individual publication, patent, or patent application was fully set forth, including any figures, herein.

SUMMARY

25 Non-limiting embodiments of the invention are described in the following labeled paragraphs:

[0001] Embodiments of the present invention encompass methods of disposing a metallic coating layer comprising a metal over at least a portion of a
30 surface of a pyrolytic graphite substrate, the metal comprising Nickel, Iron, a Nickel-Iron Alloy, or any combination thereof, and the grains of the metal being of 1 nanometers (nm) to 10000 nm in size, the metal being amorphous, or both.

[0002] Embodiments of the present invention encompass articles comprising a metallic coating layer comprising a metal disposed over at least a portion of a surface of a pyrolytic graphite substrate, the metal comprising Nickel, Iron, a Nickel-Iron Alloy, or any combination thereof, and the grains of the metal being of 1 nm to 10000 nm in size, the metal being amorphous, or both.

[0003] In embodiments of the present invention, such as, but not limited to, the method described in paragraph [0001] or the article described in paragraph [0002], the pyrolytic graphite substrate is highly oriented pyrolytic graphite, chemical vapor deposition deposited pyrolytic graphite, or a combination thereof.

[0004] In embodiments of the present invention, such as, but not limited to, the method described in paragraph [0001] or the article described in paragraph [0002], the pyrolytic graphite substrate is PYROID[®] HT, PYROID[®] SN, PYROID[®] CN, or a combination thereof.

[0005] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0004], a Nanovate[™] N2040 coating disposed over the substrate comprises the metallic coating layer.

[0006] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0005], the metallic coating layer comprises a fine grained metal of metal grain size from 2 nm to 5000 nm.

[0007] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0006], the metallic coating comprises a fine grained metal of metal grain size from 5 nm to 1000 nm.

[0008] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0007], the metallic coating comprises a fine grained metal of metal grain size from 10 nm to 500 nm.

[0009] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0005], the metallic coating comprises a fine grained metal of a metal grain size in a range having a minimum size selected from 2 nm, 5 nm, and 10 nm, and having a maximum size selected from 100 nm, 500 nm, 1000 nm, 5000 nm, and 10,000 nm.

[0010] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0009], the coating comprises an alloying addition.

5 [0011] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraph [0010], the alloying addition is selected from the group consisting of B, C, H, O, P, S, and combinations thereof.

10 [0012] In embodiments of the present invention, such as, but not limited to, the methods or articles described in paragraph [0010], the alloying addition is selected from the group consisting of Ag, Au, B, Cr, Mo, P, Pb, Pd, Rh, Ru, Sn, Zn, and combinations thereof.

15 [0013] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0012], the coating comprises solid particulates where the solid particulates are metals; metal oxides; carbides of B, Cr, Bi, Si, W, or a combination thereof; carbon; glass; polymer materials; MoS₂; or any combination thereof.

20 [0014] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraph [0013], the polymer materials are selected from the group consisting of polytetrafluoroethylene, polyvinyl chloride, polyethylene, polypropylene, acrylonitrile-butadiene-styrene, epoxy resins, and combinations thereof.

[0015] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0014], the coating comprises up to 95% by volume solid particulates.

25 [0016] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0014], the coating comprises 1% to 95% by volume solid particulates.

30 [0017] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0016], the metallic coating layer thickness is 10 μm to 50 mm.

[0018] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraph [0017], the metallic coating layer thickness is 25 μm to 25 mm.

[0019] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraph [0018], the metallic coating layer thickness is 30 μ m to 5 mm.

5 [0020] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0019], one or more intermediate coating layers are applied to the substrate before the metallic coating layer is applied.

10 [0021] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0020], at least one of the intermediate coating layer(s) comprises a metal, a polymer, or both a metal and a polymer.

15 [0022] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0021], the intermediate coating layer thickness is less than the metallic coating layer thickness by at least 20%.

[0023] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0022], the metallic coating layer, and the intermediate coating layer(s), if present, covers all of the exterior surface of the substrate.

20 [0024] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0022], the metallic coating layer, and the intermediate coating layer(s), if present, covers only a portion of the exterior surface of the substrate.

25 [0025] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0024], the thermal conductivity of the coated pyrolytic graphite is not less than the uncoated pyrolytic graphite substrate.

30 [0026] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0025], the substrate coated with the metallic coating layer exhibits a thermal conductivity of about 105% of the thermal conductivity of the uncoated substrate, or of not less than 105% of uncoated substrate and also not more than 250% of the uncoated substrate.

[0027] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0026], the substrate coated with the metallic coating layer exhibits a thermal conductivity of about 110% of the thermal conductivity of the uncoated substrate, or of not less than 110% of uncoated substrate and also not more than 250% of the uncoated substrate.

[0028] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0027], the substrate coated with the metallic coating layer exhibits a thermal conductivity of about 115% of the thermal conductivity of the uncoated substrate, or of not less than 115% of uncoated substrate and also not more than 250% of the uncoated substrate.

[0029] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0028], the substrate coated with the metallic coating layer exhibits a flexural strength greater than that of the uncoated substrate.

[0030] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0029], the substrate coated with the metallic coating layer exhibits a flexural strength of about 110% of the flexural strength of the uncoated substrate, or of not less than 110% of the uncoated substrate and also not more than 2000% of the uncoated substrate.

[0031] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0030], the metallic coating layer has a room temperature coefficient of linear thermal expansion in all directions of less than $25 \times 10^{-6} \text{ K}^{-1}$.

[0032] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0030], the metallic coating layer has a room temperature coefficient of linear thermal expansion in all directions in the range between $5.0 \times 10^{-6} \text{ K}^{-1}$ and $25 \times 10^{-6} \text{ K}^{-1}$.

[0033] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraphs [0001] – [0032], the substrate is a heat spreader.

[0034] In embodiments of the present invention, such as, but not limited to, any one of the methods or articles described in paragraph [0033], the heat spreader

is any one of those described in U.S. Patent Nos. 8,085,531, 7,859,848, 7,808,787, and 8,059,408.

BRIEF DESCRIPTION OF THE DRAWINGS

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FIG. 1 shows an example of the structure of a graphite sheet.

FIG. 2 shows a manufacturing method of highly oriented pyrolytic graphite.

10 DETAILED DESCRIPTION

Use of the singular herein, including the claims, includes the plural and vice versa unless expressly stated to be otherwise. That is, "a," "an" and "the" refer to one or more of whatever the word modifies. For example, "an article" may refer to one articles, two articles, etc. By the same token, words such as, without limitation,
15 "articles" would refer to one article as well as to a plurality of articles unless it is expressly stated or obvious from the context that such is not intended.

As used herein, words of approximation such as, without limitation, "about," "substantially," "essentially," and "approximately" mean that the word or phrase modified by the term need not be exactly that which is written but may vary from that
20 written description to some extent. The extent to which the description may vary from the literal meaning of what is written, that is the absolute or perfect form, will depend on how great a change can be instituted and have one of ordinary skill in the art recognize the modified version as still having the properties, characteristics and capabilities of the modified word or phrase. In general, but with the preceding
25 discussion in mind, a numerical value herein that is modified by a word of approximation may vary from the stated value by $\pm 15\%$, unless expressly stated otherwise.

As used herein, any ranges presented are inclusive of the end-points. For example, "a temperature between 10 °C and 30 °C" or "a temperature from 10 °C to
30 30 °C" includes 10 °C and 30 °C, as well as any temperature in between.

As used herein, a material that is described as a layer or a film (e.g., a coating) "disposed over" an indicated substrate refers to, e.g., a coating of the material deposited directly or indirectly over at least a portion of the surface of the substrate. A "layer" or a "coating" of a given material is a region of that material

whose thickness is small compared to both its length and width (e.g., the length and width dimensions may both be at least 5, 10, 20, 50, 100 or more times the thickness dimension in some embodiments). Direct depositing means that the coating is applied directly to the surface of the substrate. Indirect depositing means that the coating is applied to an intervening layer that has been deposited directly or indirectly over the substrate. A coating is supported by a surface of the substrate, whether the coating is deposited directly, or indirectly, onto the surface of the substrate. As used herein a layer need not be planar, for example, taking on the contours of an underlying substrate. Layers can be discontinuous. A layer may be of non-uniform thickness. The terms "coating", "layer", and "coating layer" will be used interchangeably and refer to a layer, film, or coating as described in this paragraph.

As used herein, the term "coating thickness" or "layer thickness" refers to the depth in a deposit direction.

The invention will now be described in detail by reference to the following specification and non-limiting examples. Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever.

Embodiments of this invention encompass methods which include applying one or more metallic coating layer(s) including a metal, or including a metal matrix composite, or including both, to a substrate comprising pyrolytic graphite. The microstructure of the metal of the metallic coating layer may be amorphous, fine-grained metal, or a combination thereof. As used herein, a "fine-grained metal" is metal having an average grain size between 1 and 5,000 nm. As used herein, the term "metal matrix composite" (MMC) is defined as particulate matter embedded in a fine-grained and/or amorphous metal matrix (metal having an average grain size between 1 and 5,000 nm). The metallic coating layers have a room temperature coefficient of linear thermal expansion (CLTE) in all directions of less than $25 \times 10^{-6} \text{ K}^{-1}$, for example, in the range between $5.0 \times 10^{-6} \text{ K}^{-1}$ and $25 \times 10^{-6} \text{ K}^{-1}$. Embodiments of the invention also encompass the coated pyrolytic graphite articles, and specifically, heat spreaders.

The coatings comprising the fine grained metals, amorphous metals, or both, and methods of applying them are described in U.S. Patent Application Publication No. 2010/0028714, published February 4, 2010, and U.S. Patent No. 8,394,507, issued on March 12, 2013. Such coatings are available as Nanovate™ coatings from Integran Technologies, Inc., Toronto, Canada. In a preferred embodiment, the coating is a Nanovate™ N2040 coating, a high strength, low coefficient of thermal expansion nanostructured Nickel-Iron coating, from Integran Technologies, Inc., Toronto, Canada.

The application of the Nanovate™ N2040 coating, a high strength, low coefficient of thermal expansion nanostructured Nickel-Iron coating, from Integran Technologies, Inc., Toronto, Canada to a substrate of pyrolytic graphite, specifically, PYROID® HT pyrolytic graphite, led to an increase of approximately 10% in the thermal conductivity of the sample. In all previous work, coating the pyrolytic graphite led to a decrease in thermal conductivity due to the increased thermal resistance of the coating. In addition, the Nanovate™ N2040 coating increased the mechanical properties, such as but without limitation, the flexural strength of the sample.

MMCs can be produced e.g. in the case of using an electroplating process by suspending particles in a suitable plating bath and incorporating particulate matter into the electrodeposit by inclusion or e.g. in the case of cold spraying by adding non-deformable particulates to the powder feed. Other methods of producing the metallic coating layers include DC or pulse electrodeposition, electroless deposition, physical vapor deposition (PVD), chemical vapor deposition (CVD), and gas condensation or the like. Some exemplary methods include those described in the following: U.S. Patent Application Publication No. 2005/0205425 A1, published on September 22, 2005; U.S. Patent No. 7,387,578, issued on June 17, 2008; and DE 10,288,323.

Solid particulate materials that may be used in forming the MCCs include metals (Ag, Al, Cu, In, Mg, Si, Sn, Pt, Ti, V, W, Zn); metal oxides (Ag₂O, Al₂O₃, SiO₂, SnO₂, TiO₂, ZnO); carbides of B, Cr, Bi, Si, W; carbon (carbon nanotubes, diamond, graphite, graphite fibers); glass; polymer materials (polytetrafluoroethylene, polyvinyl chloride, polyethylene, polypropylene, acrylonitrile-butadiene-styrene, and epoxy resins); and self-lubricating materials such as, but without limitation, MoS₂. The solid particulates may be up to 95% by volume of the coating, preferably, 1% to 95% by

volume, more preferably 5% to 75% by volume, and even more preferably from 10% to 50% by volume.

Alloying additions may be used in the metallic coating layers and are described in U.S. Patent Application Publication No. 2010/0028714, and U.S. Patent
5 No. 8,394,507, issued on March 12, 2013.

There may be one or more intermediate coating layers between the substrate surface and the metallic coating layer(s). The intermediate coating layer(s) may include, but are not limited to, a metal, a polymer, or both a metal and a polymer. Materials used in intermediate layers are described in U.S. Patent No. 8,394,507,
10 and U.S. Patent Application Publication No. 2010/0028714.

The surface of the substrate may be pre-treated by suitably roughening or texturing at least one of the surfaces to be mated to form specific surface morphologies, termed "anchoring structures" or "anchoring sites" as described in U.S. Patent No. 8,394,507.

15 With respect to the substrates used, U.S. Patent No. 8,394,507 discusses polymeric or polymer composites as substrates, but carbon substrates are not disclosed. U.S. Patent Application Publication No. 2010/0028714 discloses substrates of "carbon based materials selected from the group of graphite, graphite fibers and carbon nanotubes."

20 Graphite is made up of layer planes of hexagonal arrays or networks of carbon atoms. These layer planes of hexagonal arranged carbon atoms are substantially flat and are oriented so as to be substantially parallel and equidistant to one another. The substantially flat parallel layers of carbon atoms are referred to as basal planes and are linked or bonded together in groups arranged in crystallites.
25 Conventional or electrolytic graphite has a random order to the crystallites. Highly ordered graphite has a high degree of preferred crystallite orientation. As seen in FIG. 1, the graphite sheet 2 has hexagonal covalent bonds in a stacked crystal structure, and the graphite layers of each graphite sheet 2 are connected by van der Waals forces. The graphite sheet 2 has a thermal conductivity in the X-Y plane of
30 the graphite sheet 2 of a value greater than in the thickness direction, i.e. the Z direction. Another way of characterizing graphite is as having two principal axes, the "c" axis or direction which is generally identified as the axis or direction perpendicular to the carbon layers and the "a" axes or directions parallel to the carbon layers and transverse to the c axes. This alternative nomenclature is also shown in FIG. 1. The

“c” axis is equivalent to the Z direction, and the two “a” axes are equivalent to the X-Y plane. As used herein with reference to the axes of a graphite sheet, the term “XY” will be used interchangeably with “a” and “a-a,” and the term “Z” will be used interchangeably with “c.”

5 Graphite materials that exhibit a high degree of orientation include natural graphite and synthetic or pyrolytic graphite. Natural graphite is commercially available in the form of flakes (platelets) or as a powder. Pyrolytic graphite is produced by the pyrolysis of a carbonaceous gas on a suitable substrate at elevated temperature. Briefly, the pyrolytic deposition process may be carried out in a heated
10 furnace and at a suitable pressure, wherein a hydrocarbon gas such as methane, natural gas, acetylene etc. is introduced into the heated furnace and is thermally decomposed at the surface of a substrate of suitable composition such as graphite having any desirable shape. The substrate may be removed or separated from the pyrolytic graphite. The pyrolytic graphite may then be further subjected to thermal
15 annealing at high temperatures to form a highly oriented pyrolytic graphite commonly referred to as HOPG.

For use in heat spreaders, it is preferable to use highly oriented pyrolytic graphite having thermal conductivities more than 1,500 W/m degree K and a suitable example for use in particular is brand name PYROID[®] HT made by MINTEQ
20 International Inc. in New York, N.Y. Generally, thermal conductivity is caused by the free electrons and the lattice vibration. The high thermal conductivity (1000-2000 W/m degree K) of diamond is caused by lattice vibration, while the thermal conductivity of the extremely anisotropic HT graphite is equal to or less than diamond due to both free electron and the lattice vibration.

25 However, PYROID[®] HT pyrolytic graphite has many useful characteristics, such as the following: density 2.22 g/cc, tensile strength 28900 kPa (XY direction), elastic modulus 50 GPa (XY direction), flexural modulus 33200 MPa (XY direction), coefficient of thermal expansion 0.6×10^{-6} /degrees Celsius (XY direction), 25×10^{-6} /degrees Celsius (Z direction), thermal conductivity 1,700 Watts/m degree K (XY
30 direction), 7 Watts/in degree K (Z direction), 5.0×10^{-4} electric specific resistance Ωcm (XY direction), 0.6 Ωcm (Z direction), oxidation threshold 650 degrees Celsius (XY direction), and permeability 10^{-6} mmHg.

The thermal conductivity of PYROID[®] HT pyrolytic graphite in the XY direction compared with other materials thermal conductivity is extremely high, for example

about 6 times the values of aluminum nitride (AlN) and beryllia (BeO), and about 4 times the value of the overall thermal diffusion of the material copper (Cu) in particular.

PYROID[®] HT pyrolytic graphite is produced by the CVD method as shown in FIG. 2. In chamber 20 under vacuum by a vacuum pump 21, hydrocarbon gas supplied from cylinder 22 as raw material gas is decomposed by the gas being heated to more than 2,000 degrees Celsius by heater 23, and while minute carbon nucleus C which deposit and crystallize on substrate 24, stack and deposit in stratified formation, and PYROID[®] HT pyrolytic graphite is produced. PYROID[®] HT pyrolytic graphite is available in thicknesses of from 0.25 mm to 20 mm, and can be produce as a board of a variety of sizes as large as 300 mm square shaped structure by controlling stacking and deposit time.

MINTEQ International Inc. in New York, N.Y. also makes PYROID[®] SN (substrate nucleated) and PYROID[®] CN (continuously nucleated) grades of pyrolytic graphite also produced by the CVD process. These have lower thermal conductivity than the PYROID[®] HT pyrolytic graphite.

Embodiments of the invention also encompass the coated pyrolytic graphite articles. A specific use of the coated pyrolytic graphite is in a heat spreader. In preferred embodiments, PYROID[®] HT pyrolytic graphite is used although other grades of PYROID[®] graphite, or other grades of pyrolytic graphite may be used. In these embodiments, the heat spreader is coated on all exterior surfaces, or substantially all exterior surfaces, with one or more metallic coating layers, and optionally including one or more intermediate layers. The coating encases or encapsulates or essentially encases or encapsulates the heater spreader. Examples of heat spreaders that may be coated include any of those described in U.S. Patent Nos. 8,085,531, 7,859,848, 7,808,787, and 8,059,408. In preferred embodiments, the coating includes a Nickel-Iron alloy as a fine grained metal, amorphous metal, or combination thereof, optionally including a solid particulate, preferably a solid particulate that is a polymer material. In preferred embodiments, the fine-grained metal, if present, is of a grain size of 2 nm to 5000 nm. In preferred embodiments, the metallic layer coating thickness is 10 to 500 μ m.

In a preferred embodiment, the substrate is PYROID[®] HT pyrolytic graphite, which is used as a heat spreader, coated on all surfaces or essentially all surfaces, with a 25 to 50 μ m Nanovate[™] N2040 coating, a high strength, low coefficient of

thermal expansion nanostructured Nickel-Iron coating, from Integran Technologies, Inc., Toronto, Canada, and method of coating PYROID[®] HT pyrolytic graphite on all surfaces or essentially all surfaces with a 25 to 50 μm Nanovate[™] N2040 coating.

5 EXAMPLES

The examples presented in this section are provided by way of illustration of the current invention only and are not intended nor are they to be construed as limiting the scope of this invention in any manner whatsoever.

10 Example 1

Ten samples of PYROID[®] HT pyrolytic graphite were tested for thermal conductivity using ASTM E1461 Flash Method for Thermal Conductivity determination. In Table 1, for the first five samples, the thermal conductivity was measured in the XY orientation, and for the second five samples, the thermal
15 conductivity was measured in the Z direction. As shown in Table 1, the thermal conductivity, λ in W/m-K, ranges from 1567 to 1737 in the XY direction.

Table 1
ASTM E1461 Flash Method Thermal Conductivity Results

Sample	thickness Δx @ 25°C (mm)	bulk density ρ @ 25°C (g/cm ³)	temperature T (°C)	specific heat c_p (J/g-K)	diffusivity α (mm ² /s)	conductivity λ (W/m-K)
Pyroid-HT FAOBond Lot# 11028-FAO	3.022	2.26	25	0.761	1010	1737
Pyroid-HT Lot# 12172 Plate 2C	2.970	2.24	25	0.772	967	1672
Pyroid-HT CN Lot# 12172 Plate 9C	3.003	2.23	25	0.767	916	1567
Pyroid-HT Lot# 12172 Plate 10C	2.940	2.22	25	0.770	930	1590
Pyroid-HT Lot# 12172 Plate 17C	3.011	2.25	25	0.777	975	1705
Pyroid-HT Lot# 10062-8805- Copper Plate 5A	3.208	2.30	25	0.846	24.6	47.9
Pyroid-HT Lot# 12172-CN-8805- Copper Plate 9C	3.180	2.31	25	0.882	23.4	47.7
Pyroid-HT Lot# 12172-8805- Copper Plate 10C	3.146	2.31	25	0.807	22.1	41.2
Pyroid-HT Lot# 12172-CN-VHB- Copper Plate 9C	3.101	2.32	25	0.838	27.2	52.9
Pyroid-HT Lot# 12172-VHB- Copper Plate 10C	3.027	2.30	25	0.813	25.6	47.9

Example 2

Five samples of PYROID[®] HT pyrolytic graphite were tested for thermal conductivity using ASTM E1461 Flash Method for Thermal Conductivity determination. Samples #1 - #3 labeled UA1051, UA1052, and UA1053 were coated with a Nanovate[™] Nickel-Iron alloy coating of coating thicknesses of 25 μ m, 50 μ m,

and 50 μm , respectively. Samples #4 and #5 were uncoated. The thermal conductivity of samples #1 and #2 was determined in the XY direction. For samples #3 - #5, the thermal conductivity was determined in the Z direction. As shown in Table 2, the λ in W/m-K for each of the two coated samples measured in the XY direction, samples #1 and #2, was higher than any of the 5 uncoated samples measured in Example 1. In addition, the thermal conductivity in the Z direction was higher for coated sample #3 as compared to uncoated samples #4 and #5.

Table 2
ASTM E1461 Flash Method Thermal Conductivity Results

Sample	Thick- ness Δx @ 25°C (mm)	bulk density ρ @ 25°C (g/cm ³)	temperature T (°C)	specific heat c_p (J/g-K)	diffusivity α (mm ² /s)	conductivity λ (W/m-K)
UA1051 (#1)	2.859	2.42	25	0.743	1082	1946
UA1052 (#2)	2.895	2.47	25	0.720	982	1746
UA1053 (#3)	2.905	2.42	25	0.742	5.47	9.82
11028 (#4)	2.976	2.24	25	0.771	4.40	7.60
12172 (#5)	2.995	2.24	25	0.833	4.32	8.06

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Example 3

The flexure extension in the XY direction of 10 uncoated PYROID[®] HT pyrolytic graphite samples of 0.0625 inches in thickness and 0.5625 inches in width and 0.90 inches in length at a temperature of 73 °F and a relative humidity of 50% was determined using the ASTM D790 testing procedure. The results of 10 samples are shown in Table 3:

15

Table 3

	Flexure stress at Flex Yield Maximum Point Calculations (psi)	Yield Strain (%)	Load at Flex Yield Maximum Point Calculations (lb _f)
1	4891.09228	5.13	-9.55
2	5061.94668	5.09	-9.89
3	5132.65699	5.14	-10.02
4	4907.34853	0.41	-9.58
5	5340.14713	0.43	-10.43
6	5490.64692	0.42	-10.72
7	5059.92494	1.32	-9.88
8	5007.05097	1.24	-9.78
9	4720.94366	1.21	-9.22
10	5369.86506	1.26	-10.49
Mean	5098.16242	2.16	-9.96
Standard Deviation	240.43257	2.07130	0.46959

Example 4

The flexure extension in the Z direction of 4 uncoated PYROID[®] HT pyrolytic graphite samples of 0.0625 inches in thickness and 0.5625 inches in width and 0.90 inches in length at a temperature of 73 °F and a relative humidity of 50% was determined using the ASTM D790 testing procedure. The results of 4 samples are shown in Table 4:

Table 4

	Flexure stress at Flex Yield Maximum Point Calculations (psi)	Yield Strain (%)	Load at Flex Yield Maximum Point Calculations (lb _f)
1	7318.15204	0.79	-14.29
2	7535.14671	0.71	-14.72
3	10004.47820	-0.04	-19.54
4	9512.44969	0.40	-18.58
Mean	8592.55666	0.47	-16.78
Standard Deviation	1364.05628	0.37846	2.66417

Example 5

The flexure extension in the Z direction of 4 coated PYROID® HT pyrolytic graphite samples of 0.0625 inches in thickness and 0.5625 inches in width and 0.90 inches in length at a temperature of 73 °F and a relative humidity of 50% was determined using the ASTM D790 testing procedure. Sample #1 was coated with a Nanovate™ Nickel-Cobalt alloy coating of 25 micron in thickness. Sample #2 was coated with a Nanovate™ Nickel-Iron alloy coating of 25 micron in thickness. Sample #3 was coated with a Nanovate™ Nickel-Cobalt alloy coating of 50 micron in thickness. Sample #4 was coated with a Nanovate™ Nickel-Iron alloy coating of 50 micron in thickness. The Nanovate™ coatings were provided by and applied by Integran Technologies, Inc. The results for the 4 samples are shown in Table 5:

Table 5

	Flexure stress at Flex Yield Maximum Point Calculations (psi)	Yield Strain (%)	Load at Flex Yield Maximum Point Calculations (lbf)
1	14700.55896	0.59	-28.71
2	20956.63154	3.00	-40.93
3	37968.68219	1.57	-74.16
4	59287.40545	4.68	-115.80
Mean	33228.31954	2.46	-64.90
Standard Deviation	19961.79046	1.78007	38.98787

As seen in Table 5, the flexure stress was higher for each four of the samples in Table 5 as compared to the samples shown in Table 4. The yield strain was higher for all samples in Table 5 except sample #1.

Accordingly, it is understood that the above description of the present invention is susceptible to considerable modifications, changes and adaptations by those skilled in the art, and that such modifications, changes and adaptations are intended to be considered within the scope of the present invention, which is set forth by the appended claims.

WHAT IS CLAIMED IS:

1) A method:

disposing a metallic coating layer comprising a metal over at least a portion of a surface of a pyrolytic graphite substrate, the metal comprising Nickel, Iron, a Nickel-Iron Alloy, or any combination thereof, and the grains of the metal being of 1 nm to 10000 nm in size, the metal being amorphous, or both.

2) The method of claim 1, wherein the pyrolytic graphite is highly oriented pyrolytic graphite, chemical vapor deposition deposited pyrolytic graphite, or a combination thereof.

3) The method of claim 1, wherein the coating is a Nanovate™ N2040 coating.

4) The method of any one of claims 1 - 3, wherein the metal grain size is from 2 nm to 5000 nm.

5) The method of any one of claims 1 - 3, wherein the coating comprises an alloying addition.

6) The method of claim 5, wherein the alloying addition is selected from the group consisting of B, C, H, O, P, S, and combinations thereof.

7) The method of any one of claims 1 - 3, wherein the coating comprises solid particulate of metals; metal oxides; carbides of B, Cr, Bi, Si, W, or a combination thereof; carbon; glass; polymer materials; MoS₂; or any combination thereof.

8) The method of claim 7, wherein the coating comprises up to 95% by volume solid particulates.

9) The method of any one of claims 1 – 3, wherein the metallic layer coating thickness is 10 μm to 50 mm.

- 10) The method of any one of claims 1 – 3, wherein one or more intermediate coating layers are applied before the application of the metallic coating layer.
- 11) The method of claim 10, wherein the intermediate coating layer comprises a metal, a polymer, or both a metal and a polymer.
- 12) The method of claim 10, wherein the intermediate coating layer thickness is less than the metallic coating layer thickness.
- 13) The method of any one of claims 1 – 3, wherein the metallic coating layer covers all of the exterior surface of the substrate.
- 14) The method of any one of claims 1 – 3, wherein the metallic coating layer covers only a portion of the exterior surface of the substrate.
- 15) The method of any one of claims 1 – 3, wherein the substrate coated with the metallic coating layer exhibits a thermal conductivity not less than the uncoated substrate.
- 16) The method of any one of claims 1 – 3, wherein the substrate coated with the metallic coating layer exhibits a thermal conductivity of about 105% of the thermal conductivity of the uncoated substrate, or of not less than 105% of uncoated substrate and also not more than 250% of the uncoated substrate.
- 17) The method of any one of claims 1 – 3, wherein the substrate coated with the metallic coating layer exhibits a thermal conductivity of about 110% of the thermal conductivity of the uncoated substrate, or of not less than 110% of uncoated substrate and also not more than 250% of the uncoated substrate.
- 18) The method of any one of claims 1 – 3, wherein the substrate coated with the metallic coating layer exhibits a thermal conductivity of about 115% of the thermal conductivity of the uncoated substrate, or of not less than 115% of uncoated substrate and also not more than 250% of the uncoated substrate.

19) The method of any one of claims 1 – 3, wherein the metallic coating layer has a room temperature coefficient of linear thermal expansion in all directions of less than $25 \times 10^{-6} \text{ K}^{-1}$.

20) An article comprising:

a substrate of pyrolytic graphite;

a metallic coating layer comprising a metal deposited over at least a portion of a surface of the pyrolytic graphite substrate, the metal comprising Nickel, Iron, a Nickel-Iron Alloy, or any combination thereof, and the grains of the metal being of 1 nm to 10000 nm in size, the metal being amorphous, or both.