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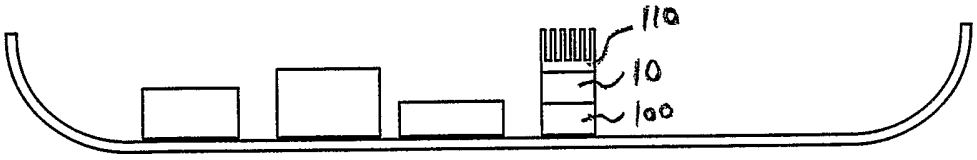

(57) Abstract: A heat riser (10) for bridging the gap between a heat source and a heat dissipation device in an electronic component, the heat riser formed of a flexible graphite article having two operative surfaces (10a, 10b), one of which is in operative contact with a surface of the heat source (100) and the other of which is in operative contact with a surface of the heat dissipation device (110).

DESCRIPTION

HEAT RISER

TECHNICAL FIELD

[0001]The present invention relates to a heat riser for bridging the gap between the heat source in an electronic device and a heat dissipation apparatus. More particularly, the inventive heat riser comprises a resin-impregnated graphite artifact formed of compressed particles of exfoliated graphite.

BACKGROUND ART

[0002]With the development of more and more sophisticated electronic devices, including those capable of increasing processing speeds and higher frequencies, having smaller size and more complicated power requirements, and exhibiting other technological advances, such as microprocessors and integrated circuits in electronic and electrical components, high capacity and response memory components such as hard drives, electromagnetic sources such as light bulbs in digital projectors, as well as in other devices such as high power optical devices, relatively extreme temperatures can be generated. However, microprocessors, integrated circuits and other sophisticated electronic components typically operate efficiently only under a certain range of threshold temperatures. The excessive heat generated during operation of these components can not only harm their own performance, but can also degrade the performance and reliability of the overall system and can even cause system failure. The increasingly wide range of environmental conditions, including temperature extremes, in which electronic systems are expected to operate, exacerbates the negative effects of excessive heat.

[0003]With the increased need for heat dissipation from microelectronic devices, thermal management becomes an increasingly important element of the design of electronic products. Both performance reliability and life expectancy of electronic equipment are inversely related to the component temperature of the equipment. For instance, a reduction in the operating temperature of a device such as a typical silicon semiconductor can

correspond to an increase in the processing speed, reliability and life expectancy of the device. Therefore, to maximize the life-span and reliability of a component, controlling the device operating temperature within the limits set by the designers is of paramount importance.

[0004]One group of relatively light weight materials suitable for use in the dissipation of heat from heat sources such as electronic components are those materials generally known as graphites, but in particular graphites such as those based on natural graphites and flexible graphite as described below. These materials are anisotropic and allow thermal dissipation devices to be designed to preferentially transfer heat in selected directions. Graphite materials are much lighter in weight than metals like copper and aluminum and graphite materials, even when used in combination with metallic components, provide many advantages over copper or aluminum when used to dissipate heat by themselves.

[0005]For instance, Tzeng, in U.S. Patent No. 6,482,520 teaches a graphite based thermal management system which includes a heat sink formed of a graphite article formed so as to have a heat collection surface and at least one heat dissipation surface. Krassowski and Chen take the Tzeng concept a step further in International Patent Application No. PCT/US02/38061, where they teach the use of high conducting inserts in a graphite base. Indeed, the use of sheets of compressed particles of exfoliated graphite (*i.e.*, flexible graphite) has been suggested as thermal spreaders, thermal interfaces and as component parts of heat sinks for dissipating the heat generated by a heat source (see, for instance, U.S. Patent Nos. 6,245,400; 6,503,626; and 6,538,892).

[0006]However, one issue which has arisen in efficient heat dissipation from electronic devices is the space requirements and limitations in some electronics, especially portable devices like laptop computers, personal digital assistants (PDAs), cell phones and the like. In these devices, it is often not feasible to place a heat sink or other heat dissipation device in direct operative contact with a heat source. Oftentimes, a gap between the heat source and dissipation device is present, especially where the heat source is located on a circuit board as is necessary for functionality and the

heat dissipation device is located at a surface of the electronic equipment in order to permit effective heat dissipation. Although conventional gap fillers and the like can be used in some instances, the gap between the heat source and dissipation device can often be too large for gap fillers commonly used. For instance, gaps can range from about 15 mm to about 50 mm, or even as high as 65 mm. Likewise, the gap in these instances can be too small for use of a conventional heat transfer device like a heat pipe, which in addition would generally not have sufficient contact surface to bridge a gap between a heat source and a heat sink (and is likely cost prohibitive for this use in any event). In these instances, a way to efficiently transfer heat from the heat source to the thermal dissipation device like a heat sink is needed.

[0007]Accordingly, there is a continuing need for a heat riser, which will function to bridge a gap between a heat source and a heat dissipation device, where conventional gap fillers and the like will not be effective.

[0008]Graphites are made up of layer planes of hexagonal arrays or networks of carbon atoms. These layer planes of hexagonally arranged carbon atoms are substantially flat and are oriented or ordered so as to be substantially parallel and equidistant to one another. The substantially flat, parallel equidistant sheets or layers of carbon atoms, usually referred to as graphene layers or basal planes, are linked or bonded together and groups thereof are arranged in crystallites. Highly ordered graphites consist of crystallites of considerable size: the crystallites being highly aligned or oriented with respect to each other and having well ordered carbon layers. In other words, highly ordered graphites have a high degree of preferred crystallite orientation. It should be noted that graphites possess anisotropic structures and thus exhibit or possess many properties that are highly directional *e.g.* thermal and electrical conductivity and fluid diffusion.

[0009]Briefly, graphites may be characterized as laminated structures of carbon, that is, structures consisting of superposed layers or laminae of carbon atoms joined together by weak van der Waals forces. In considering the graphite structure, two axes or directions are usually noted, *to wit*, the "c" axis or direction and the "a" axes or directions. For simplicity, the "c" axis or direction may be considered as the direction perpendicular to the carbon

layers. The "a" axes or directions may be considered as the directions parallel to the carbon layers or the directions perpendicular to the "c" direction. The graphites suitable for manufacturing flexible graphite sheets possess a very high degree of orientation.

[0010]As noted above, the bonding forces holding the parallel layers of carbon atoms together are only weak van der Waals forces. Natural graphites can be treated so that the spacing between the superposed carbon layers or laminae can be appreciably opened up so as to provide a marked expansion in the direction perpendicular to the layers, that is, in the "c" direction, and thus form an expanded or intumesced graphite structure in which the laminar character of the carbon layers is substantially retained.

[0011]Graphite flake which has been greatly expanded and more particularly expanded so as to have a final thickness or "c" direction dimension which is as much as about 80 or more times the original "c" direction dimension can be formed without the use of a binder into cohesive or integrated sheets of expanded graphite, *e.g.* webs, papers, strips, tapes, foils, mats or the like (typically referred to as "flexible graphite"). The formation of graphite particles which have been expanded to have a final thickness or "c" dimension which is as much as about 80 times or more the original "c" direction dimension into integrated flexible sheets by compression, without the use of any binding material, is believed to be possible due to the mechanical interlocking, or cohesion, which is achieved between the voluminously expanded graphite particles.

[0012]In addition to flexibility, the sheet material, as noted above, has also been found to possess a high degree of anisotropy with respect to thermal and electrical conductivity and fluid diffusion, comparable to the natural graphite starting material due to orientation of the expanded graphite particles and graphite layers substantially parallel to the opposed faces of the sheet resulting from very high compression, *e.g.* roll pressing. Sheet material thus produced has excellent flexibility, good strength and a very high degree of orientation.

[0013]Briefly, the process of producing flexible, binderless anisotropic graphite sheet material, *e.g.* web, paper, strip, tape, foil, mat, or the like,

comprises compressing or compacting under a predetermined load and in the absence of a binder, expanded graphite particles which have a "c" direction dimension which is as much as about 80 or more times that of the original particles so as to form a substantially flat, flexible, integrated graphite sheet. The expanded graphite particles that generally are worm-like or vermiform in appearance, once compressed, will maintain the compression set and alignment with the opposed major surfaces of the sheet. The density and thickness of the sheet material can be varied by controlling the degree of compression. The density of the sheet material can be within the range of from about 0.04 g/cm^3 to about 2.0 g/cm^3. The flexible graphite sheet material exhibits an appreciable degree of anisotropy due to the alignment of graphite particles parallel to the major opposed, parallel surfaces of the sheet, with the degree of anisotropy increasing upon roll pressing of the sheet material to increase orientation. In roll pressed anisotropic sheet material, the thickness, *i.e.* the direction perpendicular to the opposed, parallel sheet surfaces comprises the "c" direction and the directions ranging along the length and width, *i.e.* along or parallel to the opposed, major surfaces comprises the "a" directions and the thermal, electrical and fluid diffusion properties of the sheet are very different, by orders of magnitude, for the "c" and "a" directions.

DISCLOSURE OF THE INVENTION

[0014]The present invention provides a graphite-based heat riser formed from compressed particles of exfoliated graphite. More specifically, the inventive heat riser is formed of articles of epoxy impregnated graphite compressed (such as by calendering) and then cured at elevated temperatures and pressures. The resultant material exhibits unexpectedly good mechanical and thermal properties and also possesses good machinability. The thermal properties exhibited by the graphite article permit efficient transfer of heat from a heat source to a heat dissipation device such as a heat sink. Because of the efficiency of this thermal transfer, heat generated by the heat source is dissipated to a greater extent that previously anticipated.

[0015]The inventive heat riser comprises compressed particles of exfoliated graphite (sometimes referred to with the term of art "flexible graphite"). As used herein, the term "flexible graphite" also refers to sheets of pyrolytic graphite, either singly or as a laminate. The flexible graphite article employed in the inventive heat riser has an in-plane thermal conductivity substantially higher than its through-plane thermal conductivity. In other words, the article of the present invention has a relatively high (on the order of 10 or greater) thermal anisotropic ratio. The thermal anisotropic ratio is the ratio of in-plane thermal conductivity to through-plane thermal conductivity.

[0016]By forming a heat riser of flexible graphite, a heat riser article can be provided to effectively bridge the gap between a heat source and a thermal dissipation device. In addition, the inventive heat riser can be shaped to fit in the required shape, and provide a direct heat transfer path to enable optimal heat transfer.

[0017]The inventive heat riser comprises two operative surfaces, one of which is arrayed in operative contact with a heat source, such as a hard drive or electronics chip in an electronic device. Indeed, the heat riser can be placed in direct contact with the heat source; alternatively, a thermal interface or like material can be disposed between the heat riser and the heat source. The second operative surface of the inventive heat riser is placed in operative contact with a heat dissipation device like the base of a heat sink. Direct contact between the heat riser and a heat sink, or with a thermal interface therebetween, can be maintained.

[0018]Since the inventive heat riser is formed of anisotropic flexible graphite, the planes of high thermal conductivity in the heat riser can be arrayed such that heat is transmitted between the heat source and the thermal dissipation device in as efficient a manner as possible. For instance, in an isotropic material like copper or aluminum, the heat from the heat source is transmitted equally along all surfaces of the metallic material. The use of an anisotropic flexible graphite heat riser, however, permits the heat to be primarily directed from one major surface of the heat riser to the other.

[0019]The inventive heat riser is shaped to optimize thermal transfer between the heat source and the heat dissipation device, although the most common shape is as a rectangular block, with the operative surfaces comprising two opposing surfaces of the heat riser. Generally, contact between the heat riser and the heat source and/or the heat dissipation device is maintained by pressure exerted on the respective devices by clamps or other holding devices. Adhesives are undesirable since they may degrade thermal transfer, although at times adhesives can be employed if they are thermally conductive or applied as a thin enough layer to reduce the amount of thermal degradation in the transfer of heat between the heat riser and heat source and between the heat riser and heat sink.

[0020]Accordingly, it is an object of the present invention to provide a heat riser for facilitating the transfer of heat from a component of an electronic device to a heat dissipation device.

[0021]Still another object of the present invention is the provision of a heat riser having a sufficiently high thermal anisotropic ratio to function effectively for optimized heat transfer from a heat source to a heat dissipation article or material.

[0022]Yet another object of the present invention is the provision of a heat riser which can be formed in a variety of shapes and which provides heat transfer in an environment where available space is otherwise impractical.

[0023]These objects and others which will be apparent to the skilled artisan upon reading the following description, can be achieved by providing a heat riser for bridging the gap between a heat source and a heat dissipation device in an electronic device, the heat riser comprising a flexible graphite article having two operative surfaces, one of which is in operative contact with a surface of the heat source and the other of which is in operative contact with a surface of the heat dissipation device. The invention also comprises a thermal dissipation system for an electronic component which includes the inventive heat riser in combination with the heat source and heat dissipation device.

[0024]The inventive heat riser is preferably formed of a flexible graphite article which comprises at least one sheet of resin impregnated flexible

graphite pressure cured at an elevated temperature. For instance, the flexible graphite sheet can be pressure cured at a temperature of at least about 90°C and at a pressure of at least about 7 Mpa, resulting in a density greater than about 1.85 g/cm^3. In a preferred embodiment, the heat riser exhibits a thermal conductivity which is anisotropic in nature and is at least about 300 W/m°K in one plane. Most preferably, the anisotropic thermal conductivity varies by a factor of at least 15 as between a plane with a higher thermal conductivity and a plane with lower thermal conductivity.

[0025]The sheet of flexible graphite should preferably have a resin content of at least about 3% by weight, more preferably from about 5% to about 35% by weight.

[0026]The inventive heat riser should be formed such that the operative surface of the heat riser in operative contact with the thermal dissipation device generally corresponds in size and shape to the surface of the heat dissipation device contacted by the heat riser. Contrariwise, the operative surface of the heat riser in operative contact with the heat source should advantageously be larger in size than the surface of the heat source contacted by the heat riser.

[0027]It is to be understood that both the foregoing general description and the following detailed description present embodiments of the invention, and are intended to provide an overview or framework for understanding the nature and character of the invention as it is claimed. The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate various embodiments of the invention, and together with the description serve to explain the principles and operations of the invention.

[0028]Figs. 1A and 1B are perspective views of a first embodiment of the heat riser of the present invention.

[0029]Fig. 2 is a partial side plan view of a laptop having the inventive heat riser of Figs. 1A and 1B disposed between a component of the laptop and a heat dissipation device.

BEST MODE FOR CARRYING OUT THE INVENTION

[0030]As noted, the inventive heat riser is formed from compressed particles of exfoliated graphite, commonly known as flexible graphite. Graphite is a crystalline form of carbon comprising atoms covalently bonded in flat layered planes with weaker bonds between the planes. By treating particles of graphite, such as natural graphite flake, with an intercalant of, *e.g.* a solution of sulfuric and nitric acid, the crystal structure of the graphite reacts to form a compound of graphite and the intercalant. The treated particles of graphite are hereafter referred to as "particles of intercalated graphite." Upon exposure to high temperature, the intercalant within the graphite decomposes and volatilizes, causing the particles of intercalated graphite to expand in dimension as much as about 80 or more times its original volume in an accordion-like fashion in the "c" direction, *i.e.* in the direction perpendicular to the crystalline planes of the graphite. The exfoliated graphite particles are vermiform in appearance, and are therefore commonly referred to as worms. The worms may be compressed together into flexible sheets that, unlike the original graphite flakes, can be formed and cut into various shapes.

[0031]Graphite starting materials suitable for use in the present invention include highly graphitic carbonaceous materials capable of intercalating organic and inorganic acids as well as halogens and then expanding when exposed to heat. These highly graphitic carbonaceous materials most preferably have a degree of graphitization of about 1.0. As used in this disclosure, the term "degree of graphitization" refers to the value g according to the formula:

$$g = \frac{3.45 - d(002)}{0.095}$$

where d(002) is the spacing between the graphitic layers of the carbons in the crystal structure measured in Angstrom units. The spacing d between graphite layers is measured by standard X-ray diffraction techniques. The positions of diffraction peaks corresponding to the (002), (004) and (006) Miller Indices are measured, and standard least-squares techniques are employed to derive spacing which minimizes the total error for all of these peaks. Examples of highly graphitic carbonaceous materials include natural

graphites from various sources, as well as other carbonaceous materials such as graphite prepared by chemical vapor deposition, high temperature pyrolysis of polymers, or crystallization from molten metal solutions and the like. Natural graphite is most preferred.

[0032]The graphite starting materials used in the present invention may contain non-graphite components so long as the crystal structure of the starting materials maintains the required degree of graphitization and they are capable of exfoliation. Generally, any carbon-containing material, the crystal structure of which possesses the required degree of graphitization and which can be exfoliated, is suitable for use with the present invention. Such graphite preferably has a purity of at least about eighty weight percent. More preferably, the graphite employed for the present invention will have a purity of at least about 94%. In the most preferred embodiment, the graphite employed will have a purity of at least about 98%.

[0033]A common method for manufacturing graphite sheet is described by Shane *et al.* in U.S. Patent No. 3,404,061, the disclosure of which is incorporated herein by reference. In the typical practice of the Shane *et al.* method, natural graphite flakes are intercalated by dispersing the flakes in a solution containing *e.g.*, a mixture of nitric and sulfuric acid, advantageously at a level of about 20 to about 300 parts by weight of intercalant solution per 100 parts by weight of graphite flakes (pph). The intercalation solution contains oxidizing and other intercalating agents known in the art. Examples include those containing oxidizing agents and oxidizing mixtures, such as solutions containing nitric acid, potassium chlorate, chromic acid, potassium permanganate, potassium chromate, potassium dichromate, perchloric acid, and the like, or mixtures, such as for example, concentrated nitric acid and chlorate, chromic acid and phosphoric acid, sulfuric acid and nitric acid, or mixtures of a strong organic acid, *e.g.* trifluoroacetic acid, and a strong oxidizing agent soluble in the organic acid. Alternatively, an electric potential can be used to bring about oxidation of the graphite. Chemical species that can be introduced into the graphite crystal using electrolytic oxidation include sulfuric acid as well as other acids.

[0034]In a preferred embodiment, the intercalating agent is a solution of a mixture of sulfuric acid, or sulfuric acid and phosphoric acid, and an oxidizing agent, *i.e.* nitric acid, perchloric acid, chromic acid, potassium permanganate, hydrogen peroxide, iodic or periodic acids, or the like. Although less preferred, the intercalation solution may contain metal halides such as ferric chloride, and ferric chloride mixed with sulfuric acid, or a halide, such as bromine as a solution of bromine and sulfuric acid or bromine in an organic solvent.

[0035]The quantity of intercalation solution may range from about 20 to about 350 pph and more typically about 40 to about 160 pph. After the flakes are intercalated, any excess solution is drained from the flakes and the flakes are water-washed. Alternatively, the quantity of the intercalation solution may be limited to between about 10 and about 40 pph, which permits the washing step to be eliminated as taught and described in U.S. Patent No. 4,895,713, the disclosure of which is also herein incorporated by reference.

[0036]The particles of graphite flake treated with intercalation solution can optionally be contacted, *e.g.* by blending, with a reducing organic agent selected from alcohols, sugars, aldehydes and esters which are reactive with the surface film of oxidizing intercalating solution at temperatures in the range of 25°C and 125°C. Suitable specific organic agents include hexadecanol, octadecanol, 1-octanol, 2-octanol, decylalcohol, 1, 10 decanediol, decylaldehyde, 1-propanol, 1,3 propanediol, ethyleneglycol, polypropylene glycol, dextrose, fructose, lactose, sucrose, potato starch, ethylene glycol monostearate, diethylene glycol dibenzoate, propylene glycol monostearate, glycerol monostearate, dimethyl oxylate, diethyl oxylate, methyl formate, ethyl formate, ascorbic acid and lignin-derived compounds, such as sodium lignosulfate. The amount of organic reducing agent is suitably from about 0.5 to 4% by weight of the particles of graphite flake.

[0037]The use of an expansion aid applied prior to, during or immediately after intercalation can also provide improvements. Among these improvements can be reduced exfoliation temperature and increased expanded volume (also referred to as "worm volume"). An expansion aid in

this context will advantageously be an organic material sufficiently soluble in the intercalation solution to achieve an improvement in expansion. More narrowly, organic materials of this type that contain carbon, hydrogen and oxygen, preferably exclusively, may be employed. Carboxylic acids have been found especially effective. A suitable carboxylic acid useful as the expansion aid can be selected from aromatic, aliphatic or cycloaliphatic, straight chain or branched chain, saturated and unsaturated monocarboxylic acids, dicarboxylic acids and polycarboxylic acids which have at least 1 carbon atom, and preferably up to about 15 carbon atoms, which is soluble in the intercalation solution in amounts effective to provide a measurable improvement of one or more aspects of exfoliation. Suitable organic solvents can be employed to improve solubility of an organic expansion aid in the intercalation solution.

[0038]Representative examples of saturated aliphatic carboxylic acids are acids such as those of the formula $H(CH_2)_nCOOH$ wherein n is a number of from 0 to about 5, including formic, acetic, propionic, butyric, pentanoic, hexanoic, and the like. In place of the carboxylic acids, the anhydrides or reactive carboxylic acid derivatives such as alkyl esters can also be employed. Representative of alkyl esters are methyl formate and ethyl formate. Sulfuric acid, nitric acid and other known aqueous intercalants have the ability to decompose formic acid, ultimately to water and carbon dioxide. Because of this, formic acid and other sensitive expansion aids are advantageously contacted with the graphite flake prior to immersion of the flake in aqueous intercalant. Representative of dicarboxylic acids are aliphatic dicarboxylic acids having 2-12 carbon atoms, in particular oxalic acid, fumaric acid, malonic acid, maleic acid, succinic acid, glutaric acid, adipic acid, 1,5-pentanedicarboxylic acid, 1,6-hexanedicarboxylic acid, 1,10-decanedicarboxylic acid, cyclohexane-1,4-dicarboxylic acid and aromatic dicarboxylic acids such as phthalic acid or terephthalic acid. Representative of alkyl esters are dimethyl oxylate and diethyl oxylate. Representative of cycloaliphatic acids is cyclohexane carboxylic acid and of aromatic carboxylic acids are benzoic acid, naphthoic acid, anthranilic acid, p-aminobenzoic acid, salicylic acid, o-, m- and p-tolyl acids, methoxy and ethoxybenzoic acids,

acetoacetamidobenzoic acids and, acetamidobenzoic acids, phenylacetic acid and naphthoic acids. Representative of hydroxy aromatic acids are hydroxybenzoic acid, 3-hydroxy-1-naphthoic acid, 3-hydroxy-2-naphthoic acid, 4-hydroxy-2-naphthoic acid, 5-hydroxy-1-naphthoic acid, 5-hydroxy-2-naphthoic acid, 6-hydroxy-2-naphthoic acid and 7-hydroxy-2-naphthoic acid. Prominent among the polycarboxylic acids is citric acid.

[0039]The intercalation solution will be aqueous and will preferably contain an amount of expansion aid of from about 1 to 10%, the amount being effective to enhance exfoliation. In the embodiment wherein the expansion aid is contacted with the graphite flake prior to or after immersing in the aqueous intercalation solution, the expansion aid can be admixed with the graphite by suitable means, such as a V-blender, typically in an amount of from about 0.2% to about 10% by weight of the graphite flake.

[0040]After intercalating the graphite flake, and following the blending of the intercalant coated intercalated graphite flake with the organic reducing agent, the blend is exposed to temperatures in the range of 25° to 125°C to promote reaction of the reducing agent and intercalant coating. The heating period is up to about 20 hours, with shorter heating periods, *e.g.*, at least about 10 minutes, for higher temperatures in the above-noted range. Times of one half hour or less, *e.g.*, on the order of 10 to 25 minutes, can be employed at the higher temperatures.

[0041]The thusly treated particles of graphite are sometimes referred to as "particles of intercalated graphite." Upon exposure to high temperature, *e.g.* temperatures of at least about 160°C and especially about 700°C to 1000°C and higher, the particles of intercalated graphite expand as much as about 80 to 1000 or more times their original volume in an accordion-like fashion in the c-direction, *i.e.* in the direction perpendicular to the crystalline planes of the constituent graphite particles. The expanded, *i.e.* exfoliated, graphite particles are vermiform in appearance, and are therefore commonly referred to as worms. The worms may be compressed together into flexible sheets that, unlike the original graphite flakes, can be formed and cut into various shapes.

[0042]Flexible graphite sheet and foil are coherent, with good handling strength, and are suitably compressed, *e.g.* by roll pressing, to a thickness of about 0.075 mm to 3.75 mm and a typical density of about 0.1 to 1.5 grams per cubic centimeter (g/cm^3). From about 1.5-30% by weight of ceramic additives can be blended with the intercalated graphite flakes as described in U.S. Patent No. 5,902,762 (which is incorporated herein by reference) to provide enhanced resin impregnation in the final flexible graphite product. The additives include ceramic fiber particles having a length of about 0.15 to 1.5 millimeters. The width of the particles is suitably from about 0.04 to 0.004 mm. The ceramic fiber particles are non-reactive and non-adhering to graphite and are stable at temperatures up to about 1100°C, preferably about 1400°C or higher. Suitable ceramic fiber particles are formed of macerated quartz glass fibers, carbon and graphite fibers, zirconia, boron nitride, silicon carbide and magnesia fibers, naturally occurring mineral fibers such as calcium metasilicate fibers, calcium aluminum silicate fibers, aluminum oxide fibers and the like.

[0043]The above described methods for intercalating and exfoliating graphite flake may beneficially be augmented by a pretreatment of the graphite flake at graphitization temperatures, *i.e.* temperatures in the range of about 3000°C and above and by the inclusion in the intercalant of a lubricious additive, as described in International Patent Application No. PCT/US02/39749.

[0044]The pretreatment, or annealing, of the graphite flake results in significantly increased expansion (*i.e.*, increase in expansion volume of up to 300% or greater) when the flake is subsequently subjected to intercalation and exfoliation. Indeed, desirably, the increase in expansion is at least about 50%, as compared to similar processing without the annealing step. The temperatures employed for the annealing step should not be significantly below 3000°C, because temperatures even 100°C lower result in substantially reduced expansion.

[0045]The annealing of the present invention is performed for a period of time sufficient to result in a flake having an enhanced degree of expansion upon intercalation and subsequent exfoliation. Typically the time required

will be 1 hour or more, preferably 1 to 3 hours and will most advantageously proceed in an inert environment. For maximum beneficial results, the annealed graphite flake will also be subjected to other processes known in the art to enhance the degree expansion – namely intercalation in the presence of an organic reducing agent, an intercalation aid such as an organic acid, and a surfactant wash following intercalation. Moreover, for maximum beneficial results, the intercalation step may be repeated.

[0046]The annealing step of the instant invention may be performed in an induction furnace or other such apparatus as is known and appreciated in the art of graphitization; for the temperatures here employed, which are in the range of 3000°C, are at the high end of the range encountered in graphitization processes.

[0047]Because it has been observed that the worms produced using graphite subjected to pre-intercalation annealing can sometimes "clump" together, which can negatively impact area weight uniformity, an additive that assists in the formation of "free flowing" worms is highly desirable. The addition of a lubricious additive to the intercalation solution facilitates the more uniform distribution of the worms across the bed of a compression apparatus (such as the bed of a calender station conventionally used for compressing (or "calendering") graphite worms into flexible graphite sheet. The resulting sheet therefore has higher area weight uniformity and greater tensile strength. The lubricious additive is preferably a long chain hydrocarbon, more preferably a hydrocarbon having at least about 10 carbons. Other organic compounds having long chain hydrocarbon groups, even if other functional groups are present, can also be employed.

[0048]More preferably, the lubricious additive is an oil, with a mineral oil being most preferred, especially considering the fact that mineral oils are less prone to rancidity and odors, which can be an important consideration for long term storage. It will be noted that certain of the expansion aids detailed above also meet the definition of a lubricious additive. When these materials are used as the expansion aid, it may not be necessary to include a separate lubricious additive in the intercalant.

[0049]The lubricious additive is present in the intercalant in an amount of at least about 1.4 pph, more preferably at least about 1.8 pph. Although the upper limit of the inclusion of lubricous additive is not as critical as the lower limit, there does not appear to be any significant additional advantage to including the lubricious additive at a level of greater than about 4 pph.

[0050]The thus treated particles of graphite are sometimes referred to as "particles of intercalated graphite." Upon exposure to high temperature, *e.g.* temperatures of at least about 160°C and especially about 700°C to 1200°C and higher, the particles of intercalated graphite expand as much as about 80 to 1000 or more times their original volume in an accordion-like fashion in the c-direction, *i.e.* in the direction perpendicular to the crystalline planes of the constituent graphite particles. The expanded, *i.e.* exfoliated, graphite particles are vermiform in appearance, and are therefore commonly referred to as worms. The worms may be compressed together into flexible articles that, unlike the original graphite flakes, can be formed and cut into various shapes and provided with small transverse openings by deforming mechanical impact as hereinafter described.

[0051]Flexible graphite articles are coherent, with good handling strength, and are suitably compressed, *e.g.* by roll-pressing, to a thickness of about 0.075 mm to 3.75 mm and a typical density of about 0.1 to 1.5 grams per cubic centimeter (g/cc). From about 1.5-30% by weight of ceramic additives can be blended with the intercalated graphite flakes as described in U.S. Patent No. 5,902,762 (which is incorporated herein by reference) to provide enhanced resin impregnation in the final flexible graphite product. The additives include ceramic fiber particles having a length of about 0.15 to 1.5 millimeters. The width of the particles is suitably from about 0.04 to 0.004 mm. The ceramic fiber particles are non-reactive and non-adhering to graphite and are stable at temperatures up to about 1100°C, preferably about 1400°C or higher. Suitable ceramic fiber particles are formed of macerated quartz glass fibers, carbon and graphite fibers, zirconia, boron nitride, silicon carbide and magnesia fibers, naturally occurring mineral fibers such as calcium metasilicate fibers, calcium aluminum silicate fibers, aluminum oxide fibers and the like.

[0052]As noted, the flexible graphite material is treated with resin and the absorbed resin, after curing, enhances the moisture resistance and handling strength, *i.e.* stiffness, of the flexible graphite article as well as "fixing" the morphology of the article. Suitable resin content is preferably at least about 5% by weight, more preferably about 10 to 35% by weight, and suitably up to about 60% by weight. Resins found especially useful in the practice of the present invention include acrylic-, epoxy- and phenolic-based resin systems, fluoro-based polymers, or mixtures thereof. Suitable epoxy resin systems include those based on diglycidyl ether of bisphenol A (DGEBA) and other multifunctional resin systems; phenolic resins that can be employed include resole and novolac phenolics. Optionally, the flexible graphite may be impregnated with fibers and/or salts in addition to the resin or in place of the resin. Additionally, reactive or non-reactive additives may be employed with the resin system to modify properties (such as tack, material flow, hydrophobicity, *etc.*).

[0053]Alternatively, the flexible graphite sheets of the present invention may utilize particles of reground flexible graphite sheets rather than freshly expanded worms, as discussed in International Patent Application No. PCT/US02/16730. The sheets may be newly formed sheet material, recycled sheet material, scrap sheet material, or any other suitable source.

[0054]Also the processes of the present invention may use a blend of virgin materials and recycled materials.

[0055]The source material for recycled materials may be sheets or trimmed portions of sheets that have been compression molded as described above, or sheets that have been compressed with, for example, pre-calendering rolls, but have not yet been impregnated with resin. Furthermore, the source material may be sheets or trimmed portions of sheets that have been impregnated with resin, but not yet cured, or sheets or trimmed portions of sheets that have been impregnated with resin and cured. The source material may also be recycled flexible graphite proton exchange membrane (PEM) fuel cell components such as flow field plates or electrodes. Each of the various sources of graphite may be used as is or blended with natural graphite flakes.

[0056]Once the source material of flexible graphite sheets is available, it can then be comminuted by known processes or devices, such as a jet mill, air mill, blender, *etc.* to produce particles. Preferably, a majority of the particles have a diameter such that they will pass through 20 U.S. mesh; more preferably a major portion (greater than about 20%, most preferably greater than about 50%) will not pass through 80 U.S. mesh. Most preferably the particles have a particle size of no greater than about 20 mesh. It may be desirable to cool the flexible graphite sheet when it is resin-impregnated as it is being comminuted to avoid heat damage to the resin system during the comminution process.

[0057]The size of the comminuted particles may be chosen so as to balance machinability and formability of the graphite article with the thermal characteristics desired. Thus, smaller particles will result in a graphite article which is easier to machine and/or form, whereas larger particles will result in a graphite article having higher anisotropy, and, therefore, greater in-plane electrical and thermal conductivity.

[0058]Once the source material is comminuted, it is then re-expanded. The re-expansion may occur by using the intercalation and exfoliation process described above and those described in U.S. Patent No. 3,404,061 to Shane *et al.* and U.S. Patent No. 4,895,713 to Greinke *et al.*

[0059]Typically, after intercalation the particles are exfoliated by heating the intercalated particles in a furnace. During this exfoliation step, intercalated natural graphite flakes may be added to the recycled intercalated particles. Preferably, during the re-expansion step the particles are expanded to have a specific volume in the range of at least about 100 cc/g and up to about 350 cc/g or greater. Finally, after the re-expansion step, the re-expanded particles may be compressed into flexible articles, as hereinafter described.

[0060]If the starting material has been impregnated with a resin, the resin should preferably be at least partially removed from the particles. This removal step should occur between the comminuting step and the re-expanding step.

[0061]Flexible graphite materials prepared according to the foregoing description can also be generally referred to as compressed particles of exfoliated graphite. Since the materials are resin-impregnated, the resin in the sheets needs to be cured before the sheets are used in their intended applications, such as for electronic thermal management.

[0062]Flexible graphite materials are, on a microscopic level, in fact comprised of individual graphite layers. These individual layers of graphite within the flexible graphite materials are not stacked close enough and with the proper crystal stacking sequence to have the same degree of orientation as individual crystals of graphite. Therefore, this material has reduced thermal conductivity in the plane of the sheet as compared to pure individual crystals of graphite. For instance, single crystals of graphite will exhibit a thermal conductivity of about 2000 W/m°K in plane and 10 out of plane. Flexible graphite sheets of the sort above described will typically exhibit a thermal conductivity of about 100-250 W/m°K in plane and about 6-9 W/m°K out of plane.

[0063]According to the invention, resin-impregnated flexible graphite materials prepared as described above are compressed to the desired thickness and shape, commonly a thickness of about 0.35 mm to 0.5 mm, at which time the impregnated flexible mats have a density of about 1.4 g/cm^3 to about 1.9 g/cm^3.

[0064]In a typical resin impregnation step, the flexible graphite material is passed through a vessel and impregnated with the resin system from, *e.g.* spray nozzles, the resin system advantageously being "pulled through the mat" by means of a vacuum chamber. Typically, but not necessarily, the resin system is solvated to facilitate application into the flexible graphite. The resin is thereafter preferably dried, reducing the tack of the resin and the resin-impregnated article.

[0065]One type of apparatus for continuously forming resin-impregnated and compressed flexible graphite materials is shown in International Publication No. WO 00/64808, the disclosure of which is incorporated herein by reference.

[0066]Following the compression step (such as by calendering), the impregnated materials are cut to suitable-sized pieces and placed in a press, where they are cured at an elevated temperature. The temperature should be sufficient to ensure that the lamellar structure is densified at the curing pressure, while the thermal properties of the structure are not adversely impacted. Generally, this will require a temperature of at least about 90°C, and generally up to about 200°C. Most preferably, cure is at a temperature of from about 150°C to 200°C. The pressure employed for curing will be somewhat a function of the temperature utilized, but will be sufficient to ensure that the lamellar structure is densified without adversely impacting the thermal properties of the structure. Generally, for convenience of manufacture, the minimum required pressure to densify the structure to the required degree will be utilized. Such a pressure will generally be at least about 7 megapascals (Mpa, equivalent to about 1000 pounds per square inch), and need not be more than about 35 Mpa (equivalent to about 5000 psi), and more commonly from about 7 to about 21 Mpa (1000 to 3000 psi). The curing time may vary depending on the resin system and the temperature and pressure employed, but generally will range from about 0.5 hours to 2 hours. After curing is complete, the composites are seen to have a density of at least about 1.8 g/cm^3 and commonly from about 1.8 g/cm^3 to 2.0 g/cm^3.

[0067]Although the formation of sheets through calendaring or molding is the most common method of formation of the flexible graphite materials useful in the practice of the present invention, other forming methods can also be employed. For instance, the exfoliated graphite particles can be compression molded into a net shape or near net shape. Thus, if the end application requires an article, such as a heat sink or heat spreader, assuming a certain shape or profile, that shape or profile can be molded into the flexible graphite article, before or after resin impregnation. Cure would then take place in a mold assuming the same shape; indeed, in the preferred embodiment, compression and curing will take place in the same mold. Machining to the final shape can then be effected.

[0068]Likewise, it is also feasible that expansion of the particles of intercalated graphite can take place *in situ* in the compression mold, rather than by passing the graphite particles through a flame, followed by compression, resin impregnation and cure.

[0069]The temperature- and pressure-cured graphite/resin composites of the present invention provide for the first time a graphite-based composite material having in-plane thermal conductivity rivaling or exceeding that of copper, at a fraction of the weight of copper, and which exhibits in-plane thermal conductivity of about 300 W/m°K or higher, and an anisotropic ratio of at least about 15 (that is, the thermal conductivity varies by a factor of at least 15 as between a plane with a higher thermal conductivity and a plane with lower thermal conductivity).

[0070]The inventive heat riser can be formed in the shape desired. Alternatively, the inventive heat riser can be formed as a laminate of individual flexible graphite articles, most preferably, flexible graphite sheets, with or without an adhesive between laminate layers. Non-graphite layers may be included in the laminate stack, although this may necessitate the use of adhesives, which can be disadvantageous, since it can slow thermal dissipation across the plane of the laminate stack. Such non-graphite layers may include metals, plastics or other non-metallics such as fiberglass or ceramics.

[0071]As noted above, the thusly-formed sheets of compressed particles of exfoliated graphite are anisotropic in nature; that is, the thermal conductivity of the sheets is greater in the in-plane, or "a" directions, as opposed to the through-sheet, or "c" direction. In this way, the anisotropic nature of the graphite sheet directs the heat along the planar direction of the heat riser (*i.e.*, in the "a" direction along the graphite sheet). Such a sheet generally has a thermal conductivity in the in-plane direction of at least about 140, more preferably at least about 200, and most preferably at least about 300 W/m°K and in the through-plane direction of no greater than about 20, more preferably no greater than about 10, and most preferably no greater than about 6 W/m°K. Thus, the heat riser has a thermal anistropic ratio (that is, the ratio of in-plane thermal conductivity to through-plane

thermal conductivity) of no less than about 10 and most preferably at least about 15.

[0072]The cross-sectional shape and area of the operative surface of the inventive heat riser which abuts the heat dissipation device should correspond as closely as possible to the cross-sectional shape and area of the base of the heat dissipation device, in order to facilitate thermal transfer between the heat riser and the heat dissipation device. The cross-sectional shape and area of the operative surface of the heat riser which abuts the heat source can be greater than the surface of the heat source against which the heat riser abuts. This permits some thermal spreading across the heat riser, and permits greater thermal dissipation from the heat source through the heat riser to the heat sink or other thermal dissipation device.

[0073]Referring now to the drawings, and particularly to Figs. 1A and 1B, an embodiment of the heat riser of the present invention is shown and generally designated by the numeral 10. Heat riser 10 comprises a graphite block having operative surfaces 10a and 10b formed as a laminate of sheets of compressed particles of exfoliated graphite (the individual sheet making up the laminate are not shown). One operative surface 10b of heat riser 10 is positioned in operative contact with a heat source 100 while the other operative surface 10a is in operative contact with a heat dissipation device, such as a heat sink 110, as illustrated in Fig. 2, such that heat generated by heat source 100 is transferred to heat dissipation device 110 through heat riser 10 and is thereby dissipated.

[0074]Thus, by use of the present invention, effective heat dissipation can be accomplished even where a gap between the heat source and heat dissipation device is too great to be bridged by conventional gap fillers and the like. These functions cannot be accomplished by more traditional materials like copper or aluminum which, because of their high density, are often undesirable for weight-sensitive applications.

[0075]All cited patents, patent applications and publications referred to in this application are incorporated by reference.

[0076]The invention thus being described, it will be obvious that it may be varied in many ways. Such variations are not to be regarded as a departure

from the spirit and scope of the present invention and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

CLAIMS

What is claimed is:

1. A heat riser for bridging the gap between a heat source and a heat dissipation device in an electronic device, the heat riser comprising a flexible graphite article having two operative surfaces, one of which is in operative contact with a surface of the heat source and the other of which is in operative contact with a surface of the heat dissipation device.

2. The heat riser of claim 1, wherein the flexible graphite article comprises at least one sheet of resin impregnated flexible graphite pressure cured at an elevated temperature.

3. The heat riser of claim 2, wherein the flexible graphite sheet is pressure cured at a temperature of at least about 90°C and at a pressure of at least about 7 Mpa.

4. The heat riser of claim 1, which exhibits a thermal conductivity which is anisotropic in nature and is at least about 300 W/m°K in one plane.

5. The heat riser of claim 4, wherein the anisotropic thermal conductivity varies by a factor of at least 15 as between a plane with a higher thermal conductivity and a plane with lower thermal conductivity.

6. The heat riser of claim 2, wherein the pressure cured flexible graphite sheet has a density greater than about 1.85 g/cm^3.

7. The heat riser of claim 2, wherein the sheet of flexible graphite has a resin content of at least about 3% by weight.

8. The heat riser of claim 7, wherein the sheet of flexible graphite has a resin content of from about 5% to about 35% by weight.

9. The heat riser of claim 1, wherein the operative surface of the heat riser in operative contact with the thermal dissipation device generally corresponds in size and shape to the surface of the heat dissipation device contacted by the heat riser.

10. The heat riser of claim 9, wherein the operative surface of the heat riser in operative contact with the heat source is larger in size than the surface of the heat source contacted by the heat riser.

11. A thermal dissipation system for an electronic component, the system comprising a heat source and a heat dissipation device, and heat riser

disposed between the heat source and heat dissipation device, the heat riser comprising a flexible graphite article having two operative surfaces, one of which is in operative contact with a surface of the heat source and the other of which is in operative contact with a surface of the heat dissipation device.

12. The system of claim 11, wherein the flexible graphite article comprises at least one sheet of resin impregnated flexible graphite pressure cured at an elevated temperature.

13. The system of claim 12, wherein the flexible graphite sheet is pressure cured at a temperature of at least about 90°C and at a pressure of at least about 7 Mpa.

14. The system of claim 11, which exhibits a thermal conductivity which is anisotropic in nature and is at least about 300 W/m°K in one plane.

15. The system of claim 14, wherein the anisotropic thermal conductivity varies by a factor of at least 15 as between a plane with a higher thermal conductivity and a plane with lower thermal conductivity.

16. The system of claim 12, wherein the pressure cured flexible graphite sheet has a density greater than about 1.85 g/cm^3.

17. The system of claim 12, wherein the sheet of flexible graphite has a resin content of at least about 3% by weight.

18. The system of claim 17, wherein the sheet of flexible graphite has a resin content of from about 5% to about 35% by weight.

19. The system of claim 11, wherein the operative surface of the heat riser in operative contact with the thermal dissipation device generally corresponds in size and shape to the surface of the heat dissipation device contacted by the heat riser.

20. The system of claim 19, wherein the operative surface of the heat riser in operative contact with the heat source is larger in size than the surface of the heat source contacted by the heat riser.

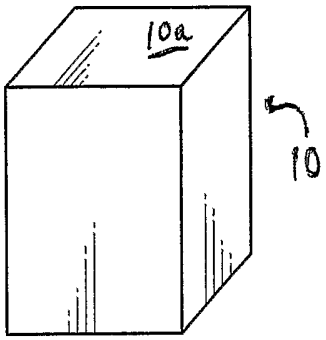

FIG. 1A

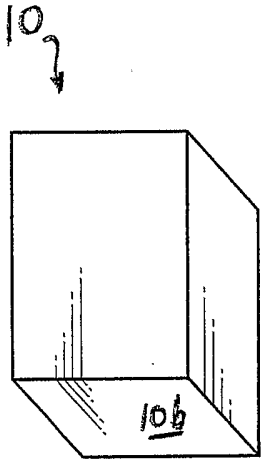

FIG. 1B

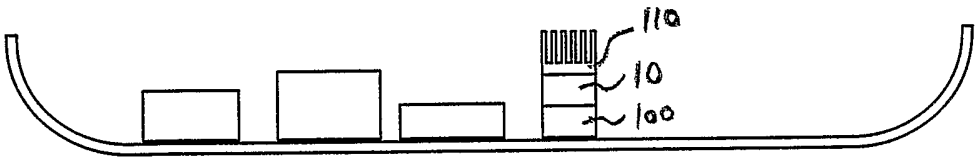

FIG. 2