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(54) **COATINGS TO RESIST HIGH-TEMPERATURE OXIDATION IN A THERMAL ENERGY STORAGE SYSTEM**

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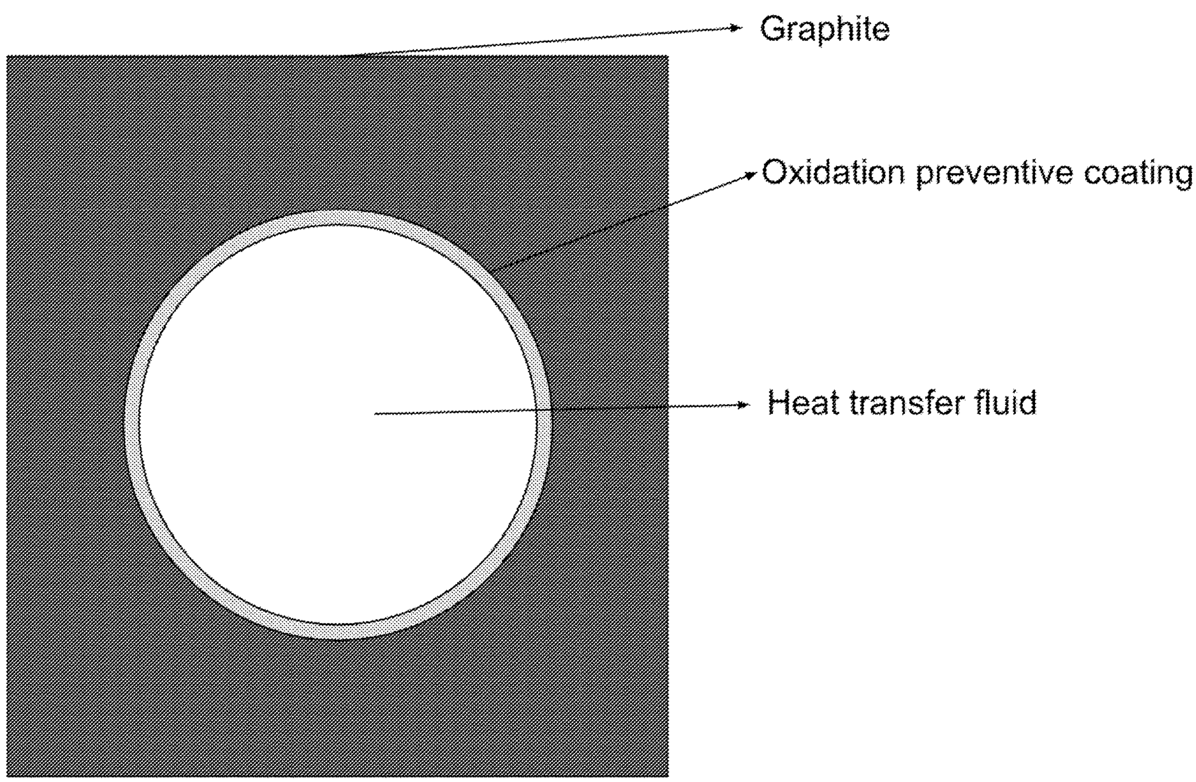
(57) **ABSTRACT**

Internal passages of a graphite thermal storage mass are treated with an anti-oxidizing coating to increase the life of installed thermal storage systems, reducing operation and maintenance costs.



Thermal Battery System and Stirling Engine

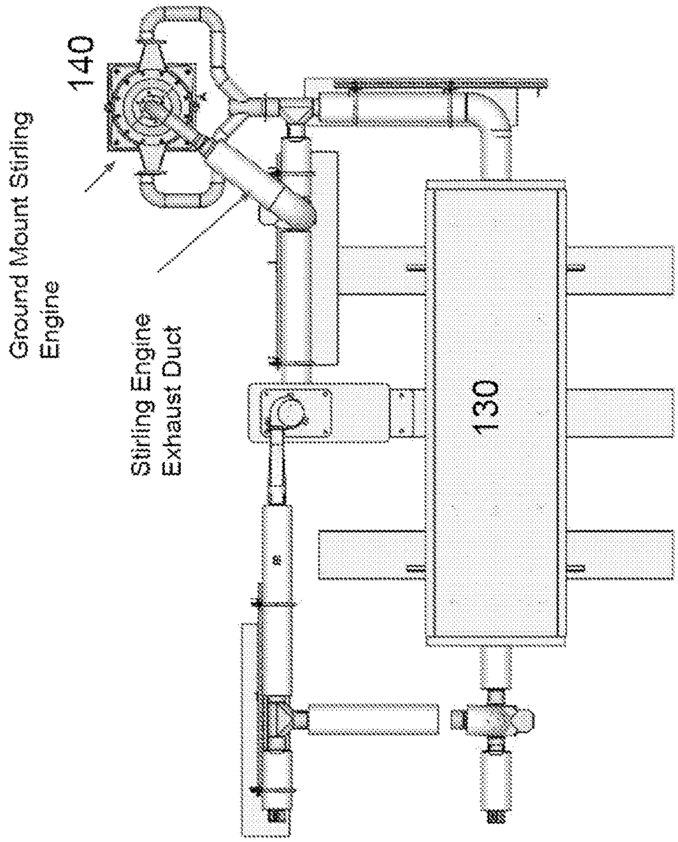


Fig. 1B

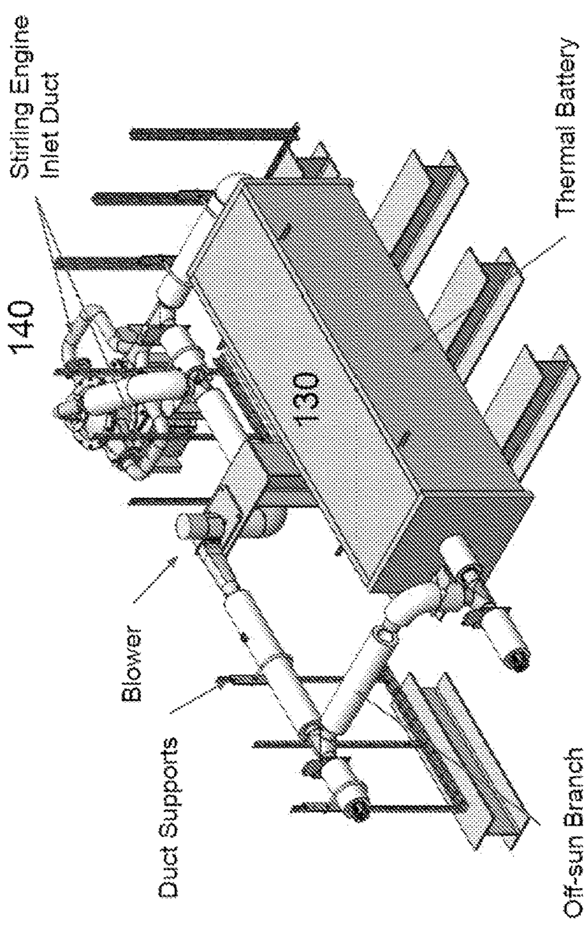


Fig. 1A

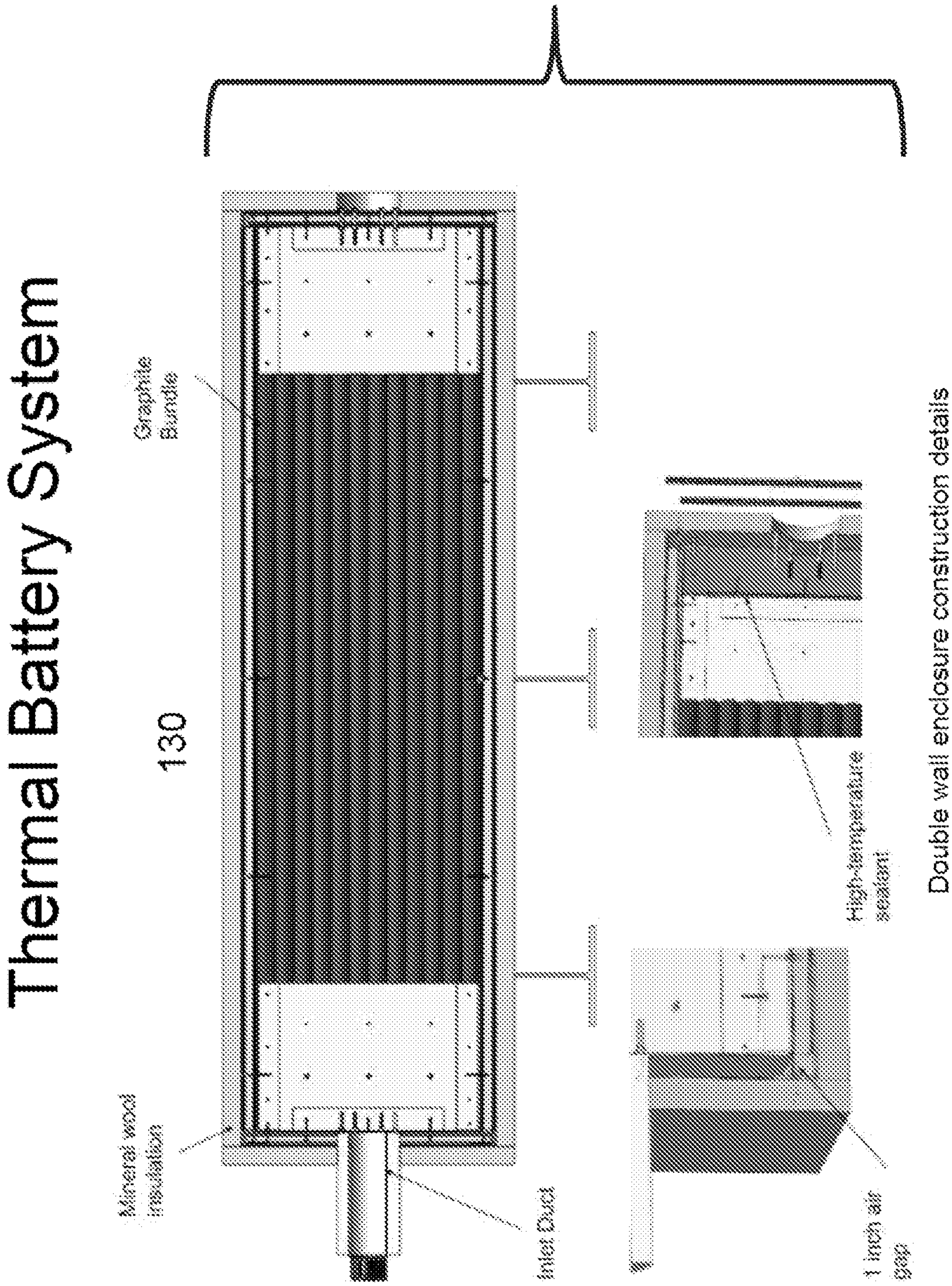

Thermal Battery System
130
Graphite Bundle
Mineral wool insulation
Inlet Duct
High-temperature sealant
1 inch air gap
Double wall enclosure construction details

Fig. 2

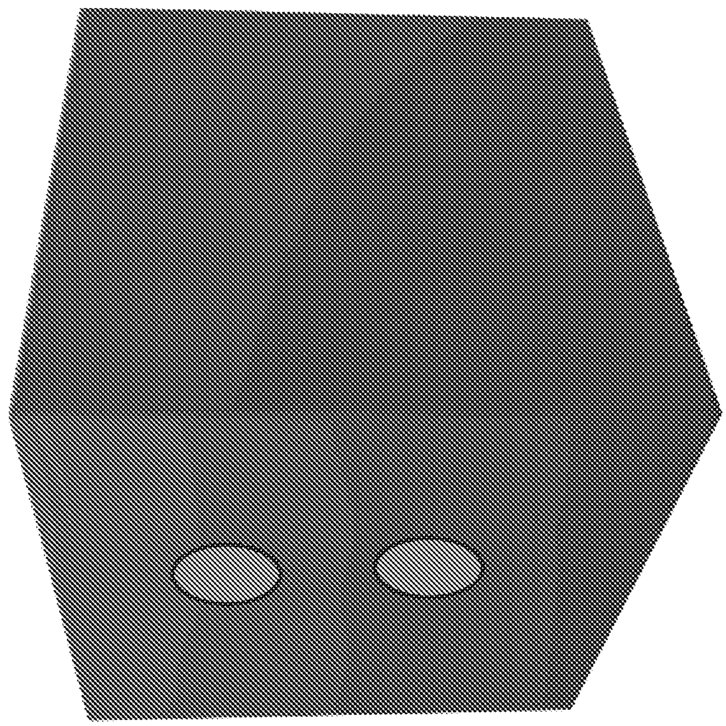


Figure 3

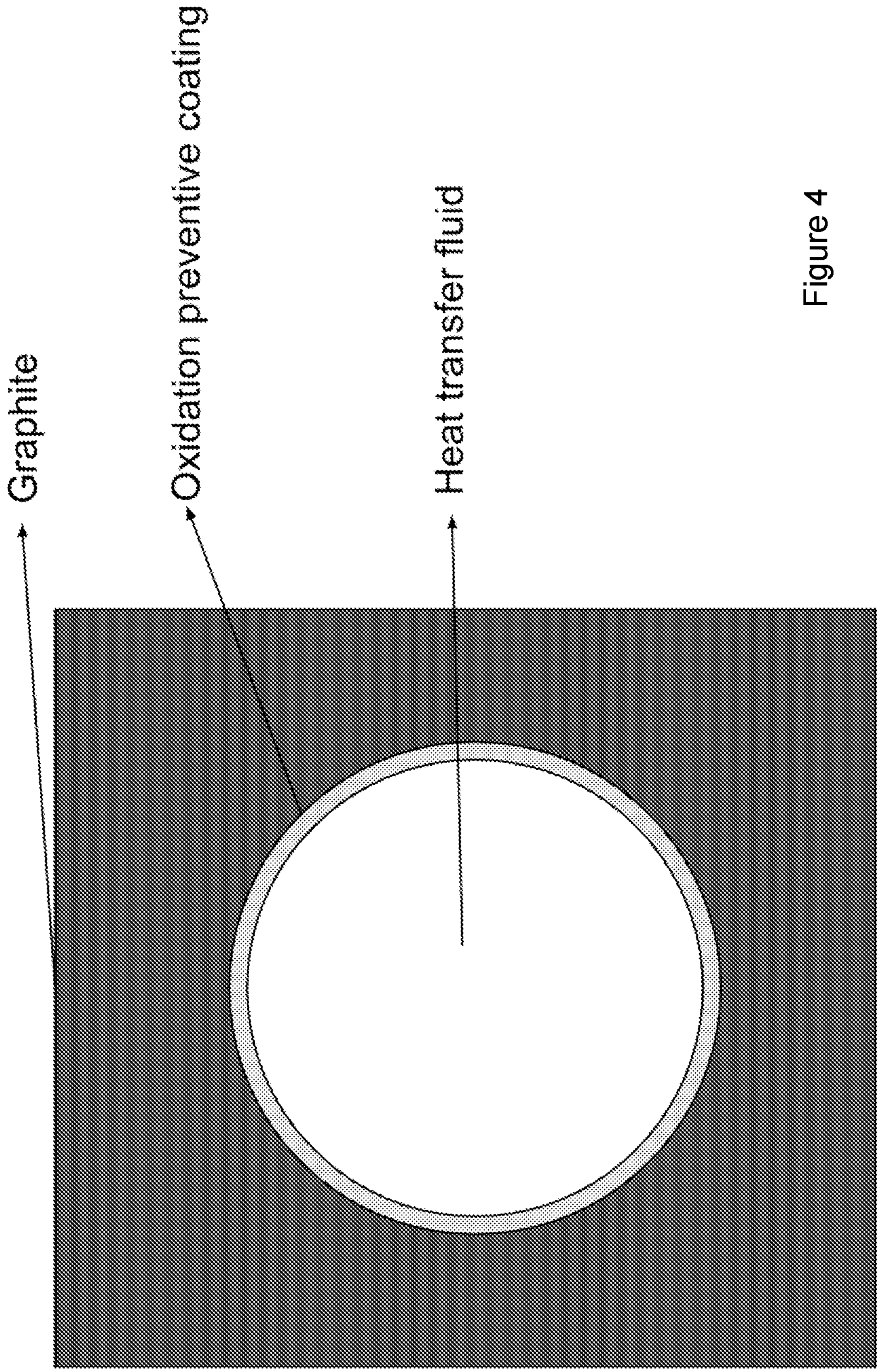

Graphite
Oxidation preventive coating
Heat transfer fluid

Figure 4

COATINGS TO RESIST HIGH-TEMPERATURE OXIDATION IN A THERMAL ENERGY STORAGE SYSTEM

CROSS-REFERENCES TO RELATED APPLICATIONS

[0001] This application claims benefit of U.S. Provisional Patent Application No. 63/555,006 filed Feb. 17, 2024, which is incorporated herein by reference in its entirety and for all purposes.

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

FIELD

[0002] The technology herein relates to storage of thermal energy such as from solar collectors. More particularly, the technology herein relates to minimizing, preventing, resisting and/or protecting against high temperature oxidation at heat extraction and/or other surfaces of graphite and other masses used to store thermal energy through use of a surface treatment such as a coating.

BACKGROUND

[0003] As "clean" energy solutions are more in demand, some are developing and using solar thermal collectors that collect heat from the sun's rays. Unlike a furnace or boiler that can activate and operate on demand, a solar thermal collector collects heat only when it is exposed to the sun's rays. Little or no heat is collected between sunset and sunrise, or when clouds and weather such as rainy days interfere with solar collection. Also, the amount of solar thermal energy that can be collected during active sunlight may be impacted by time of day, the season, the weather and other factors. Meanwhile, however, many typical loads such as building heating systems, electrical generators and the like may require energy during periods when the solar thermal collector is collecting little or no energy.

[0004] A solution is to store thermal energy during times when the solar thermal collector is actively collecting thermal energy, and to use the stored thermal energy during times when the solar thermal collector is not collecting enough energy to meet the demand of the load(s). For this reason, thermal energy storage systems ("TESS") or thermal batteries have become a valuable area of technological development. Many different technologies have been used to store thermal energy, including molten salt, steam, molten aluminum, hot silicon or sand, miscibility gap alloys, and others. See e.g., Gil et al, "State of the art on high temperature thermal energy storage for power generation" published in Renewable and Sustainable Energy Reviews Volume 14, Issue 1, January 2010, Pages 31-72; Parameshwaran et al, Sustainable thermal energy storage technologies for buildings: A review, Renewable and Sustainable Energy Reviews Volume 16, Issue 5, June 2012, Pages 2394-2433; Bauer et al, Thermal Energy Storage Materials And Systems, Annual Review of Heat Transfer (2012) pages 131-177 DOI: 10.1615/AnnualRevHeatTransfer.2012004651.

While much work has been done in the past, further improvements are possible and desirable. In particular, what is needed is a compact, rugged, cost-effective thermal storage that can be deployed as part of an outdoor or other solar thermal collection facility.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] FIGS. **1**A, **1**B show respective views of a thermal storage and thermal engine system.

[0006] FIG. **2** shows an example of a thermal battery system.

[0007] FIG. **3** shows an example of a thermal battery block.

[0008] FIGS. **4** show example illustrations of coating of a passage within a graphite block.

DETAILED DESCRIPTION OF NON-LIMITING EMBODIMENTS

[0009] The example technology herein uses an anti-oxidation coating(s) to protect internal and/or external surfaces of a thermal storage from oxidation resulting from heat transfer fluid passing through the channels that can cause oxidation and/or oxidation arising from direct impingement of solar radiation in a solar thermal absorber application.

[0010] Example non-limiting technology herein provides a surface oxidation resistant graphite mass or block for use in a graphite-based or other thermal storage system. The oxidation preventing or oxidation reduction coating used in example embodiments increases the life of installed thermal storage systems, reducing operation and maintenance costs.

[0011] An embodiment provides a graphite or clay mass having an internal passage enabling a heat transporting medium to flow through the mass, the internal passage having an internal surface in contact with the heat transporting medium, the internal surface being treated with an anti-oxidation coating. The external surface(s) of the mass may also be treated with an anti-oxidation coating. Such coatings thereby protect against both oxidation resulting from heat transfer fluid passing through the channels that can cause oxidation and oxidation arising from direct impingement of solar radiation in a solar thermal absorber application.

[0012] FIGS. **1**A-**1**B show an example thermal storage **130** coupled to a thermal load such as a thermal engine **140** e.g., a Stirling engine. The thermal storage **130** supplies thermal energy to the thermal load to operate the thermal load, e.g., to generate mechanical power and/or electricity.

[0013] In this example, the thermal storage **130** can store thermal energy for on-demand use (e.g., when clouds obscure the sun and/or after dark and before sunrise). Ducting and a blower can be used to transfer thermal energy to/from the thermal storage **130**. For example, ducting and a (re) circulation system can supply heat from one or more solar collectors to the thermal storage **130**, and ducting and a (re) circulation system can also supply heat from the thermal storage to a conventional thermal engine **140**. The thermal storage or battery **130** can be any size and shape and can have any number of inlets and outlets.

[0014] FIG. **2** shows an example thermal storage **130** comprising a graphite or other heat retaining mass disposed within an insulated housing or enclosure. In the example shown, the heat-retaining mass can be housed within a thermally insulative housing and isolated from the housing and the outer environment by insulative housing walls (e.g., double wall construction with air gaps between), air gaps between the heat retaining mass and the housing inner wall, mineral wool or other insulation, high temperature sealant and other such measures. This allows the heat retaining mass to retain very large quantities of heat for relatively long time periods. Heat retained by the heat-retaining mass can be output to a Stirling engine and/or any other thermal load. Air gaps, mineral wool insulation and high temperature sealant may be used to thermally isolate the heat-retaining mass to minimize heat loss. Inlet and outlet ducts are used to circulate the transport medium through the heat-retaining mass to add heat to and remove heat from the mass. A processor-based control system, thermal sensors and a pump or blower may be used to automatically control the rate at which the transport medium circulates to and through and/or around the heat-retaining mass.

[0015] In one example embodiment, the heat-retaining mass can comprise or consist of graphite. Graphite is a crystalline form of carbon (C) that comprises stacked layers of graphene. Thermal properties are strongly influenced by the anisotropy of the graphite crystal. Graphite is generally impossible to melt—that it, it can be heated to very high temperatures without entering the liquid state. This makes graphite a good candidate for storing large amounts of heat. Graphite also has good heat transfer properties and high thermal conductivity with a low coefficient of thermal expansion—meaning it can be heated to very high temperatures without expanding much. Graphite is therefore an excellent material to store thermal energy. However, graphite is known to lose its surface cohesion when exposed to high temperatures. This characteristic has in the past discouraged the use of graphite in certain shapes and forms for high temperature energy storage.

[0016] Other example materials for the mass may include clay, aluminum, concrete, or other materials that maintain solid state during and after heating.

[0017] Example embodiments herein provide oxidation prevention or reduction coatings (via e.g., electrochemical deposition or bulk exposure inside a coating environment) for a heat-retaining mass or object such as a pre fabricated block (of various shapes). Such coating can have the ability to prevent or reduce the oxidation process without compromising the cohesiveness and the inherent heat spreading capability of the heat-retaining mass.

[0018] FIG. **3** shows that in one example embodiment, the heat retaining mass may comprise a compression-molded block shaped for example as a cube or rectangular prism. In one embodiment, certain interior and/or exterior surfaces of the block are coated with an oxidation prevention or reduction coating to prevent, substantially prevent, resist and/or reduce occurrences or effects of oxidation of the graphite when exposed to air. FIG. **4** shows a coating disposed on an inner passage surface. In the example shown, there can be multiple passages (e.g, a heat inlet passage and a heat outlet passage for separate heat supply and draw circuits) and each such passage can be coated internally with a protective coating. Additionally, coatings can be applied to the exterior surface(s) of the block to reduce or prevent oxidation of the exterior surface(s).

[0019] In other embodiments as shown in FIG. **2**, the mass can comprise a bundle of rods or tubes. Once again, the inner and/or outer surfaces of such ods or tubes are coated with an oxidation prevention or reduction coating to prevent, substantially prevent, resist and/or reduce occurrences or effects of oxidation of the graphite when exposed to air.

[0020] In one embodiment, the passages within the FIG. **3** mass pass through the mass from one side to the other to provide passages through the mass through which thermal transfer fluid such as air or other gas may flow. These passages through the mass may communicate with external pipes or ducts that carry a heated medium such as a heated gas (for example air, CO2, Helium, or any other suitable gas) or liquid. In such examples, the inner surfaces of such internal passages through the mass are likely to experience the highest temperature and the highest temperatures, making them more likely to oxidize. Coatings on the interior surfaces of such passages within the mass may be used to increase heat retention and/or transfer efficiency. For example, if air is used as the heated medium, then an oxidizing prevention or reduction coating may be uniformly applied onto the inner surfaces of the passages within the gmass to reduce oxidizing within the mass.

[0021] For example, FIG. **3** thus may use multiple pipes or ducts in the form of a plenum or manifold that may deliver heat derived from one or multiple sources such as one or multiple solar thermal collectors. The plenum or manifold shown may distribute heat uniformly through a block or other shaped mass to prevent cracking or other uneven heating effects. An outlet on the other side of the block or other mass may be used to deliver heat to a thermal load such as a Stirling engine. A medium pump such as a gas blower may be used to transport heat into and out of the block or other mass. In one embodiment, the heated medium can be recirculated through the block or other mass to add heat to or remove heat from the block or other mass.

Example Coatings to Protect Against Oxidation

[0022] Coatings with high thermal conductivity with similar thermal expansion coefficient like graphite are preferred for oxidation prevention or reduction coatings. Coating with high thermal conductivity materials in suspension with qualities such as high temperature stability, corrosion resistance and ability to form protective oxide layer, good adhesion to the surface, low surface tension, and resistance to thermal cycling are preferred.

[0023] More particularly, suitable coatings for preventing or reducing oxidation at high temperatures may exhibit several properties in example embodiments:

[0024] 1. High Temperature Stability: The coating remains stable and maintains its structural integrity at elevated temperatures. This prevents degradation or breakdown of the coating under thermal stress; and/or

[0025] 2. Corrosion Resistance: The coating resists chemical reactions with the surrounding environment, particularly oxygen and other corrosive elements that can lead to oxidation. This resistance helps in preserving the substrate material; and/or

[0026] 3. Oxide Layer Formation: Ideally, the coating facilitates formation of a protective oxide layer on the graphite surface when exposed to high temperatures. This layer acts as a barrier, preventing or reducing further oxidation of the underlying material; and/or

[0027] 4. Adhesion: Strong adhesion to the substrate ensures that the coating stays in place, even under conditions of thermal expansion and contraction. Good adhesion prevents the coating from peeling or cracking; and/or.

[0028] 5. Thermal Cycling Resistance: The coating should be able to withstand repeated cycles of heating and cooling without deteriorating. Thermal cycling can cause stress on the coating-substrate interface, and a robust coating can mitigate potential damage; and/or

[0029] 6. Chemical Compatibility: The coating should be compatible with the specific environment it is exposed to. Different high-temperature applications may involve varying chemical compositions, and the coating should be resistant to these chemicals; and/or

[0030] 7. Thickness Control: Example embodiments control the thickness of the coating. Too thin, and it may not provide sufficient protection; too thick, and it might affect thermal conductivity or lead to other issues; and/or

[0031] 8. Uniformity: A uniform coating ensures consistent protection across the entire surface. Variations in thickness or coverage could result in localized vulnerability to oxidation; and/or

[0032] 9. Ease of Application: Practical considerations include how easily the coating can be applied to complex shapes or surfaces, as well as the feasibility of applying it in the specific industrial or manufacturing setting. A wide variety of coatings have been used as conventional techniques for the preservation of carbon products against oxidation, such as SiC, TiC, TiN, Si_3N_4, B_4C, SiO_2, $ZrSiO_4$, ZrO_2, HfC—ZrC—SiC, Al_2O_3, mullite, hexagonal-BN, LaB_6—$MoSi_2$—ZrB_2, $MoSi_2$—SiC, ZrB_2—ZrC—SiC and ZrB_2. See e.g., Ghazvini et al, "SiC/nano α-Al_2O_3 Double-Layer Coating on Graphite Component via Pack Cementation and Electrophoretic Deposition" Oct. 21, 2020//doi.org/10.21203/rs.3.rs-94021/v1 retrieved from assets.researchsquare.com/files/rs-94021/v1/529466d8-e034-4605-b3d4-7e4lee532c29.pdf?c=1637243691. Some of these may be suitable for reducing or protecting against oxidation of a hot graphite surface. Additionally, the following non-limiting examples may meet some or all of the above criteria and/or aspects thereof.

Example I

[0033] An example anti-oxidizing coating is applied to the graphite surfaces of a thermal storage mass described above. The coating is formulated as described in U.S. Pat. No. 4,711,666 and comprises a binder/suspension liquid for use in preparing a protective coating to substantially prevent oxidation of graphitic materials up to at least 1000 degrees Centigrade, comprising a substantially pure colloidal silica solution of a selected volume; a substantially pure mono-aluminum phosphate solution of a selected volume, said selected volume of said mono-aluminum phosphate solution being from about 0.54 to about 1.86 times said selected volume of said colloidal silica solution, said colloidal silica solution and said mono-aluminum phosphate solution being intimately mixed; and substantially pure ethyl alcohol of a selected volume, said selected volume of said ethyl alcohol being from about 0.05 to 0.45 times the combined selected volumes of said colloidal silica solution and said mono-aluminum phosphate solution, said ethyl alcohol intimately mixed with said mixed colloidal silica solution and mono-aluminum phosphate solution.

Example II

[0034] An example oxidation prevention or reduction coating is applied to the graphite surfaces of a thermal storage mass described above. The coating is formulated as described in Zhu et al, "Oxidation resistant SiC coating for graphite materials" Carbon Volume 37, Issue 9, 1999, Pages 1475-1484; doi.org/10.1016/S0008-6223(99)00010-X

Example III

[0035] An example coating that protects against oxidation is applied to the graphite surfaces of a thermal storage mass described above. The coating is formulated based on titanium diboride as in Graphi-Coat 623 Graphite Oxidation Resistant Coating, Grade ARMC-623, Aremco Products, Inc.

Example IV

[0036] An example coating is applied to the graphite surfaces of a thermal storage mass described above. The coating is formulated as in Yang et al, "A multi-layered SiC coating to protect graphite spheres from high temperature oxidation in static air", Corrosion Science Volume 183, 1 May 2021, 109325//doi.org/10.1016/j.corsci.2021.109325.

Example V

[0037] An example coating is applied to the graphite surfaces of a thermal storage mass described above. The coating is formulated as described in Ghazvini et al above, wherein SiC is coated on graphite via pack cementation method and then a layer of nano α-Al_2O_3 is coated on it through the electrophoretic deposition (EPD) method to improve the oxidation resistance at high temperatures. This alumina coating is further sintered for 20 minutes at 1350° C. e.g., in a microwave furnace to densify and close oxygen permeation paths.

Example VI

[0038] A graphite block treated as described above is used in conjunction with a means or mechanism for preventing (or reducing the amount of) oxygen that reaches the heated surface(s) of the graphite thermal storage mass. Such a means or mechanism could in one embodiment comprise a nitrogen or other gas injection system in combination with seals that prevent oxygen from entering a chamber in which the graphite mass is disposed.

Example VII

[0039] A block or other shaped mass of clay, concrete, aluminum or other heat retaining/absorbing material has fluid passages defined therethrough communicating with a source and/or sink of heated fluid. The interior surfaces of the fluid passages are coated with a coating that reduces or prevents degradation of such interior surfaces from the fluid passaging therethrough.

Example VIII

[0040] A block or other shaped mass of clay, concrete, aluminum or other heat retaining/absorbing material defines an exterior surface(s) on which collected solar energy is focused to heat the mass. The exterior surface is coated with a coating that reduces or prevents degradation of such surface(s) due to heating in the presence of air or other gas.

Example IX

[0041] A block or other shaped mass of clay, concrete, aluminum or other heat retaining/absorbing material defines an interior surface(s) on which collected solar energy is focused to heat the mass. The interior surface is coated with a coating that reduces or prevents degradation of such surface(s) due to heating in the presence of air or other gas.

Example X

[0042] A block or other shaped mass of clay, concrete, aluminum or other heat retaining/absorbing material defines both interior surface(s) and exterior surface(s). Collected solar energy may be focused on such surfaces to heat the mass and/or a fluid may flow in contact with such interior and/or exterior surface(s). The surface(s) are each coated with a coating that reduces or prevents degradation of such surface(s) due to the presence of oxygen or other degrading gas or fluid.

[0043] All patents and publications cited herein are incorporated by reference.

[0044] While the technology herein has been described in connection with exemplary illustrative non-limiting embodiments, the invention is not to be limited by the disclosure. The invention is intended to be defined by the claims and to cover all corresponding and equivalent arrangements whether or not specifically disclosed herein.

We claim:

1. Methods substantially as shown and described herein.

2. Systems substantially as shown and described herein.

3. A graphite mass having an internal passage enabling a heat transporting medium to flow through the graphite mass, the internal passage having an internal surface in contact with the heat transporting medium, the internal surface being treated with an anti-oxidation coating.

* * * * *