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(54) MICROSTRUCTURAL SURFACE INCORPORATION OF PHASE CHANGE MATERIALS FOR THERMAL MANAGEMENT

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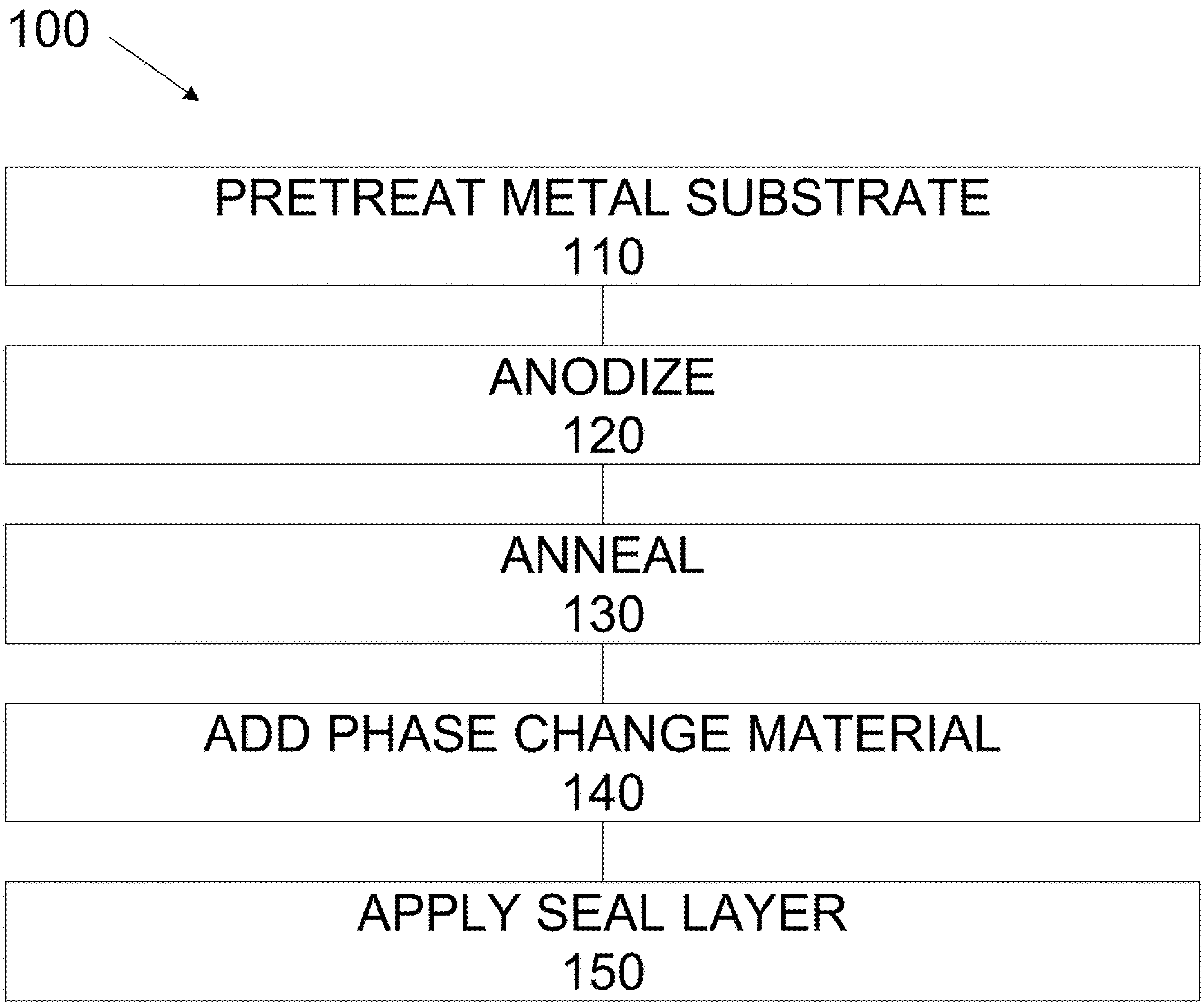
(57) ABSTRACT

A process for protecting an article from thermal damage includes anodizing a metallic surface of the article to form an anodic layer containing a metal oxide; annealing the anodic layer; introducing a phase change material to pores defined by the anodic layer; and applying a seal layer to seal the phase change material within the pores.



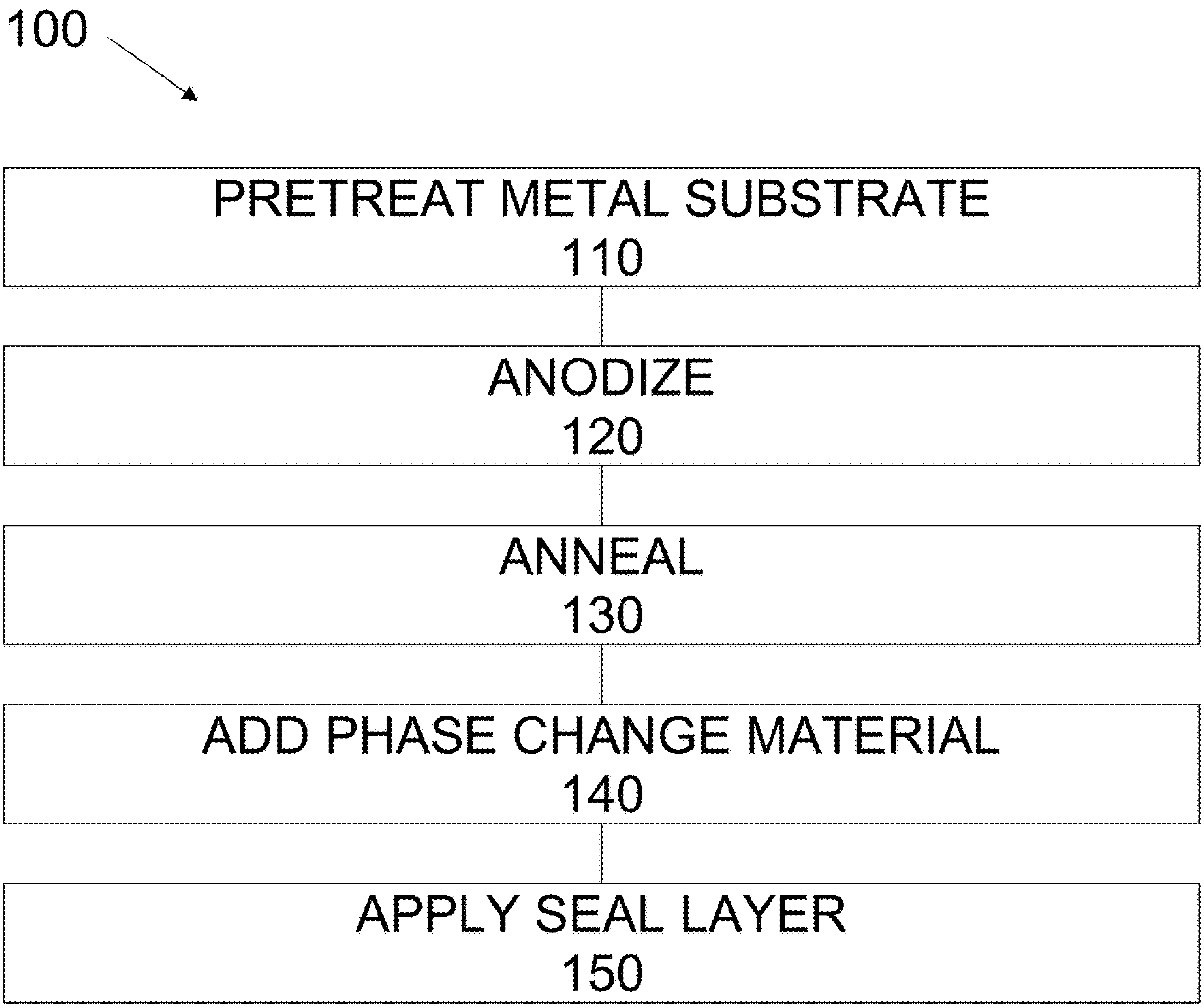

100
PRETREAT METAL SUBSTRATE
110
ANODIZE
120
ANNEAL
130
ADD PHASE CHANGE MATERIAL
140
APPLY SEAL LAYER
150

FIG. 1

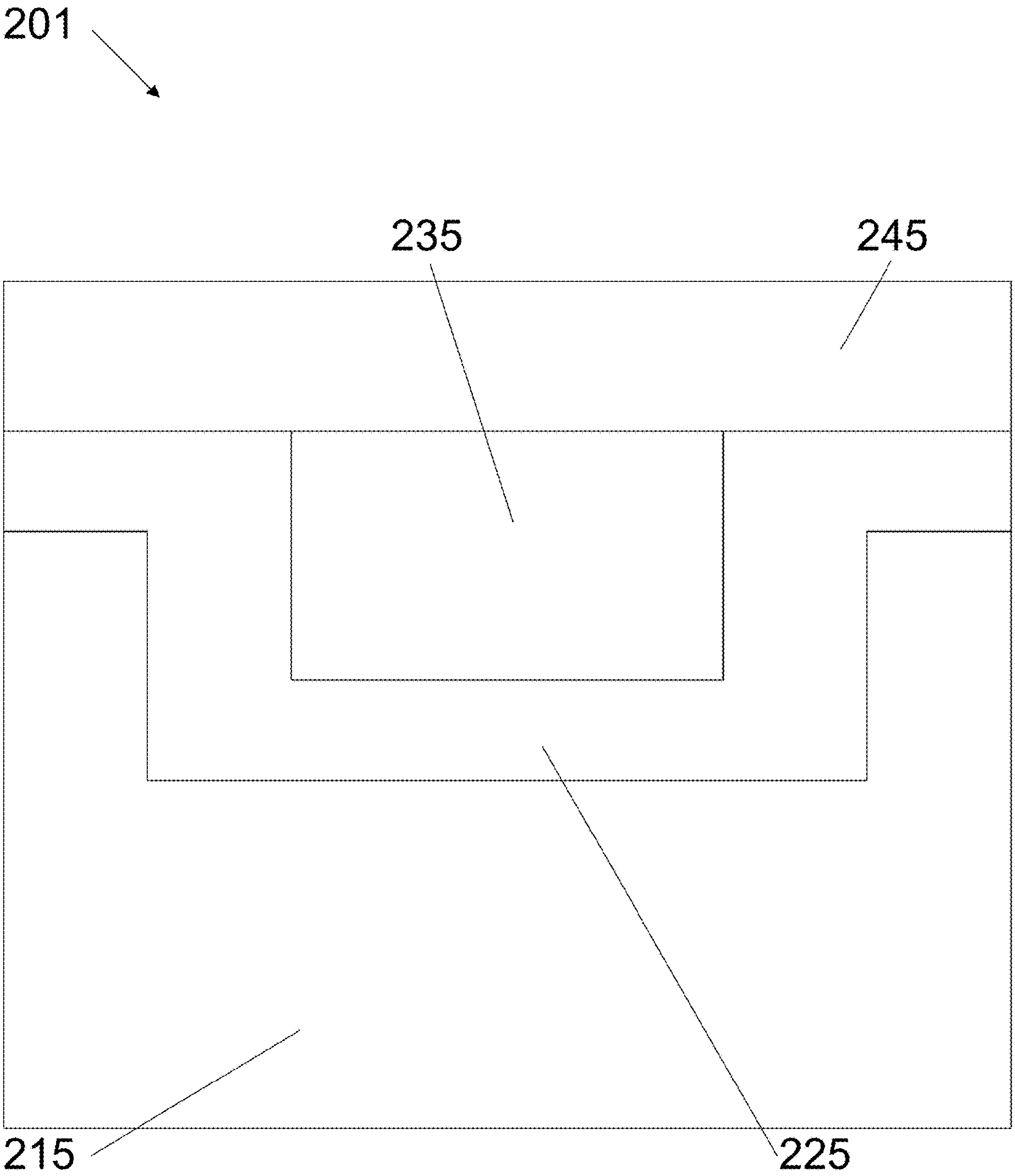


FIG. 2

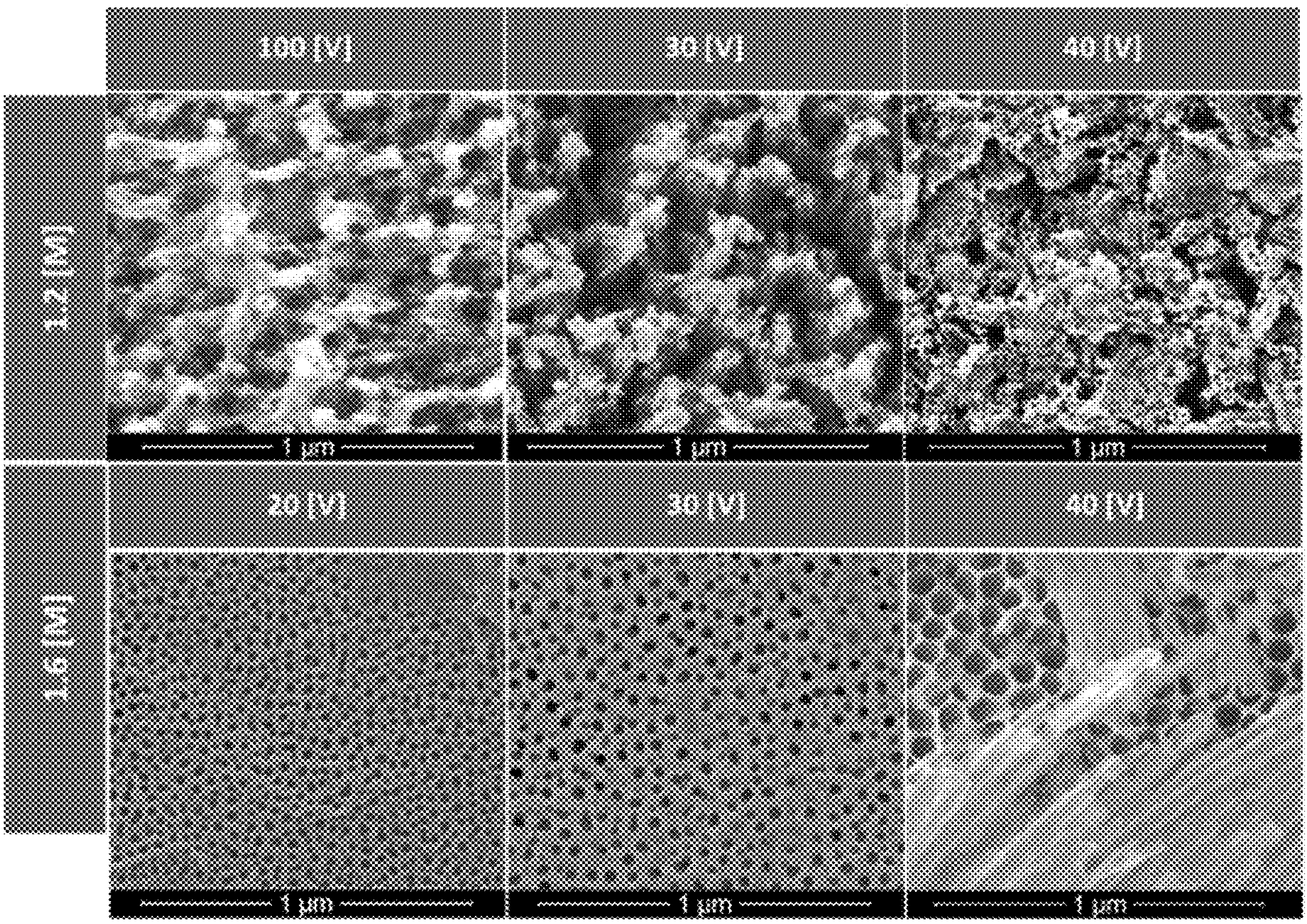


FIG. 3

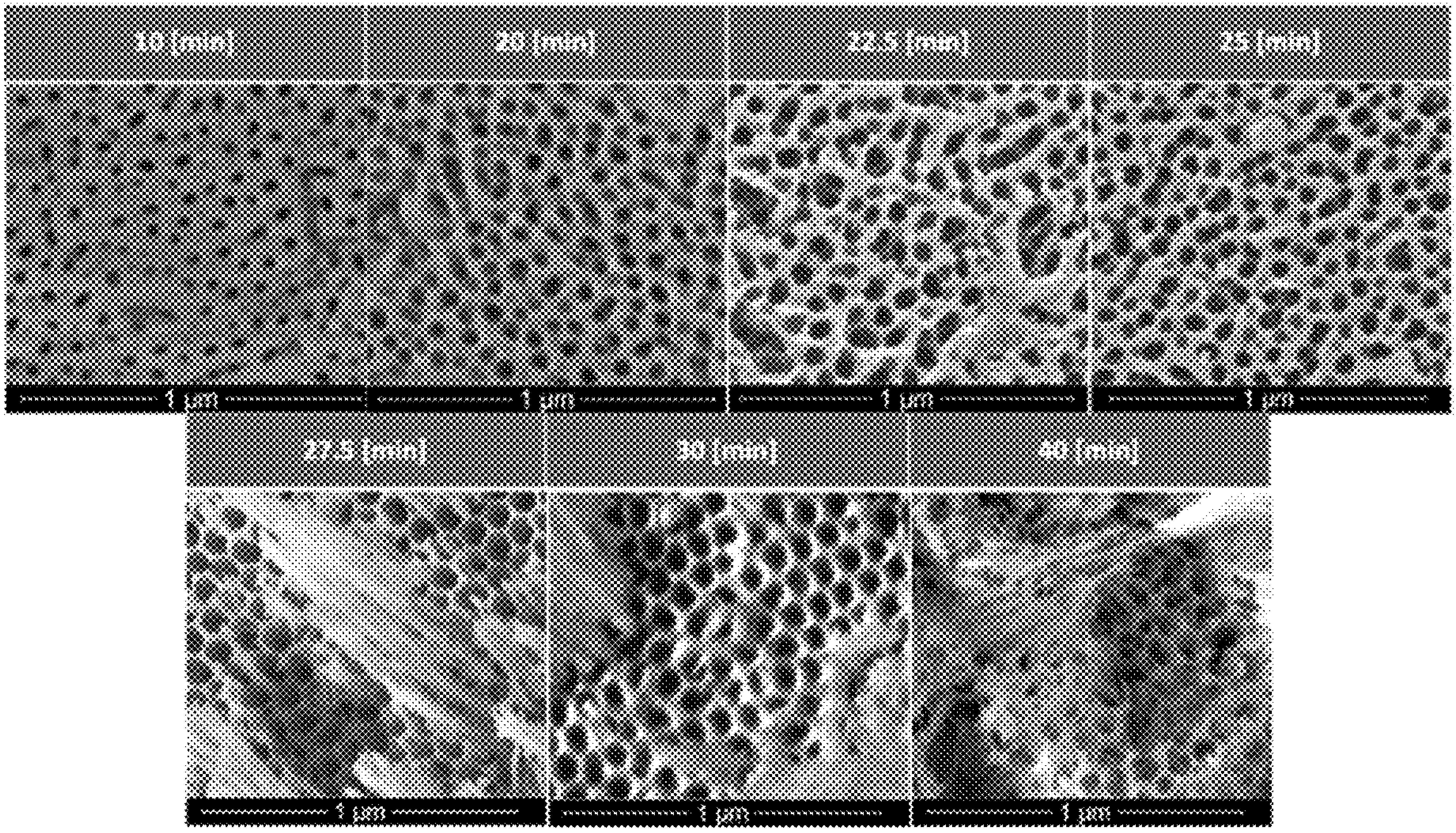

10 [min]
20 [min]
22.5 [min]
25 [min]
1 µm
1 µm
1 µm
1 µm
27.5 [min]
30 [min]
40 [min]
1 µm
1 µm
1 µm

FIG. 4

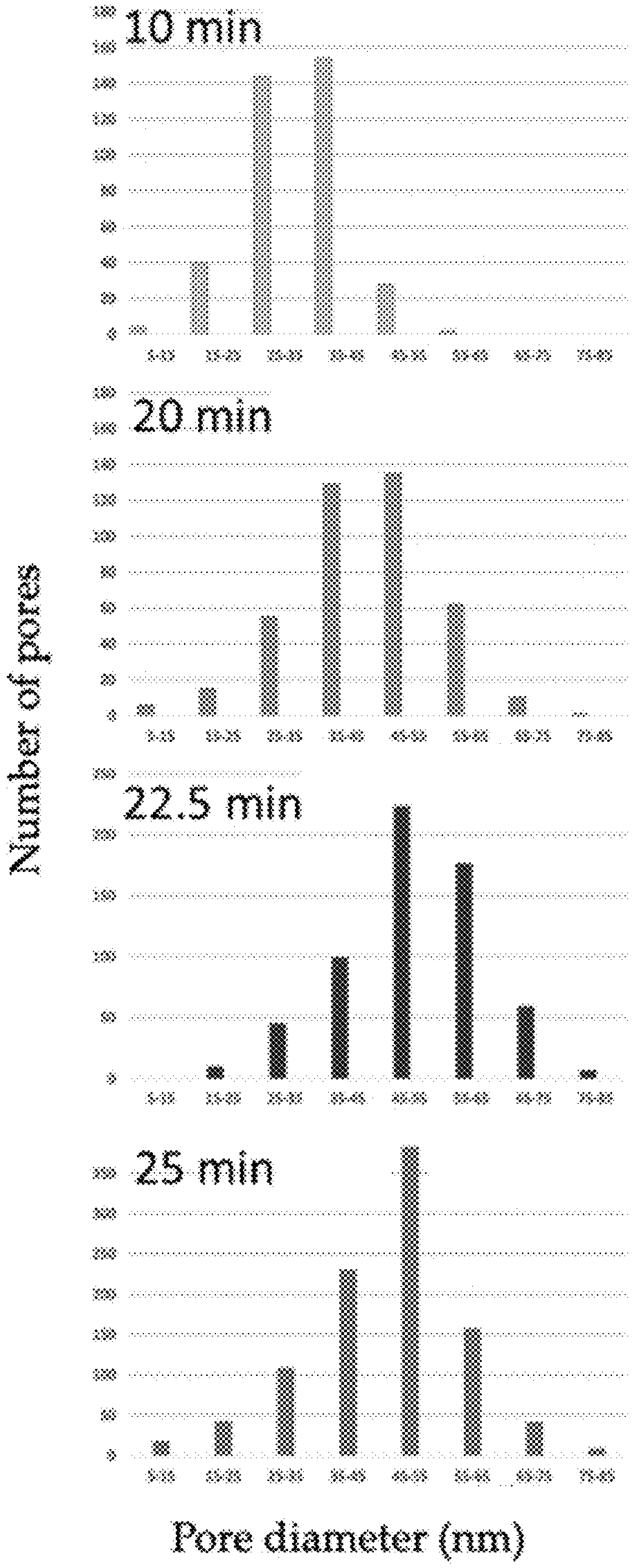


FIG. 5

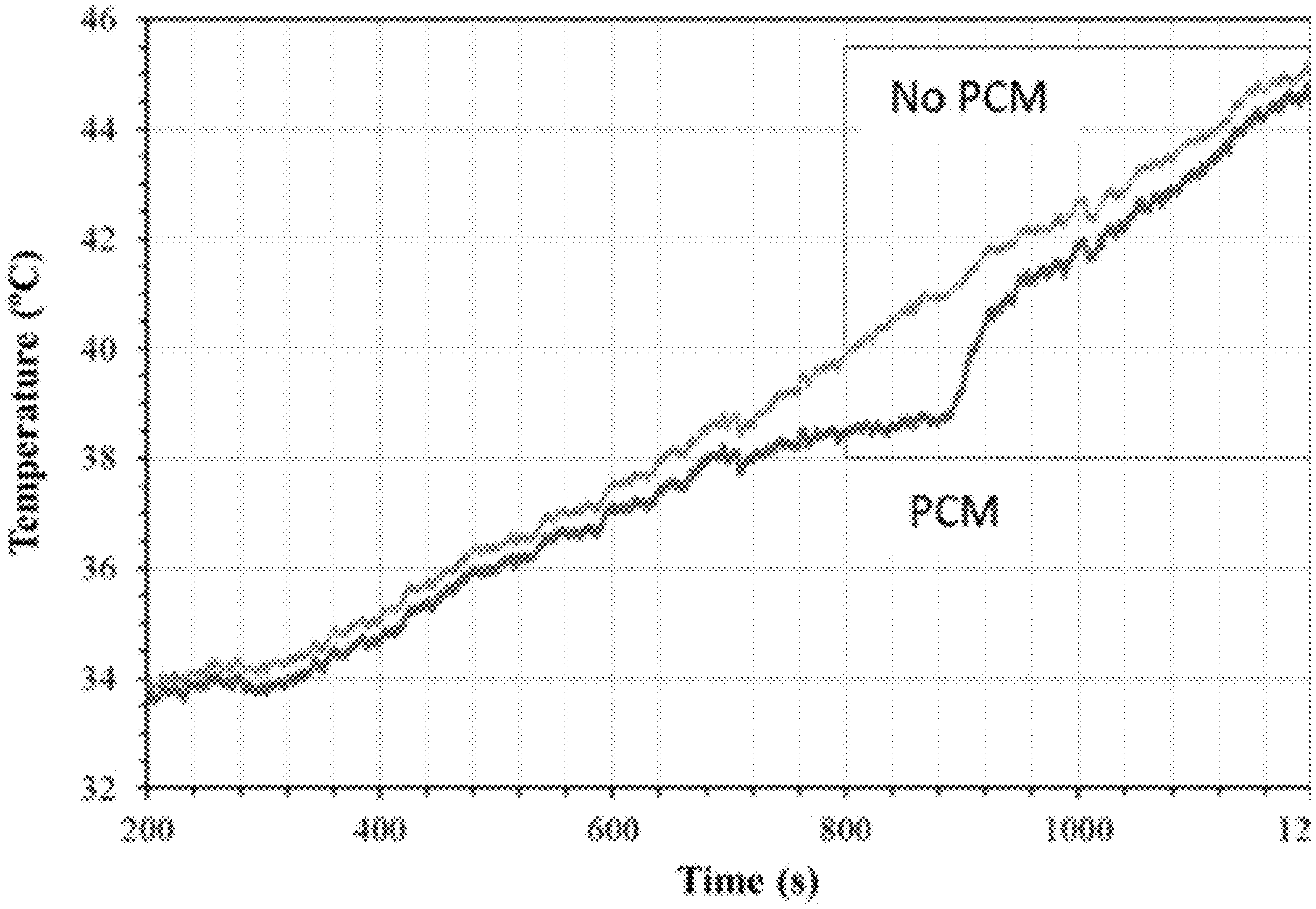

46
44
42
40
38
36
34
32
Temperature (°C)
200
400
600
800
1000
12
Time (s)
No PCM
PCM

FIG. 6

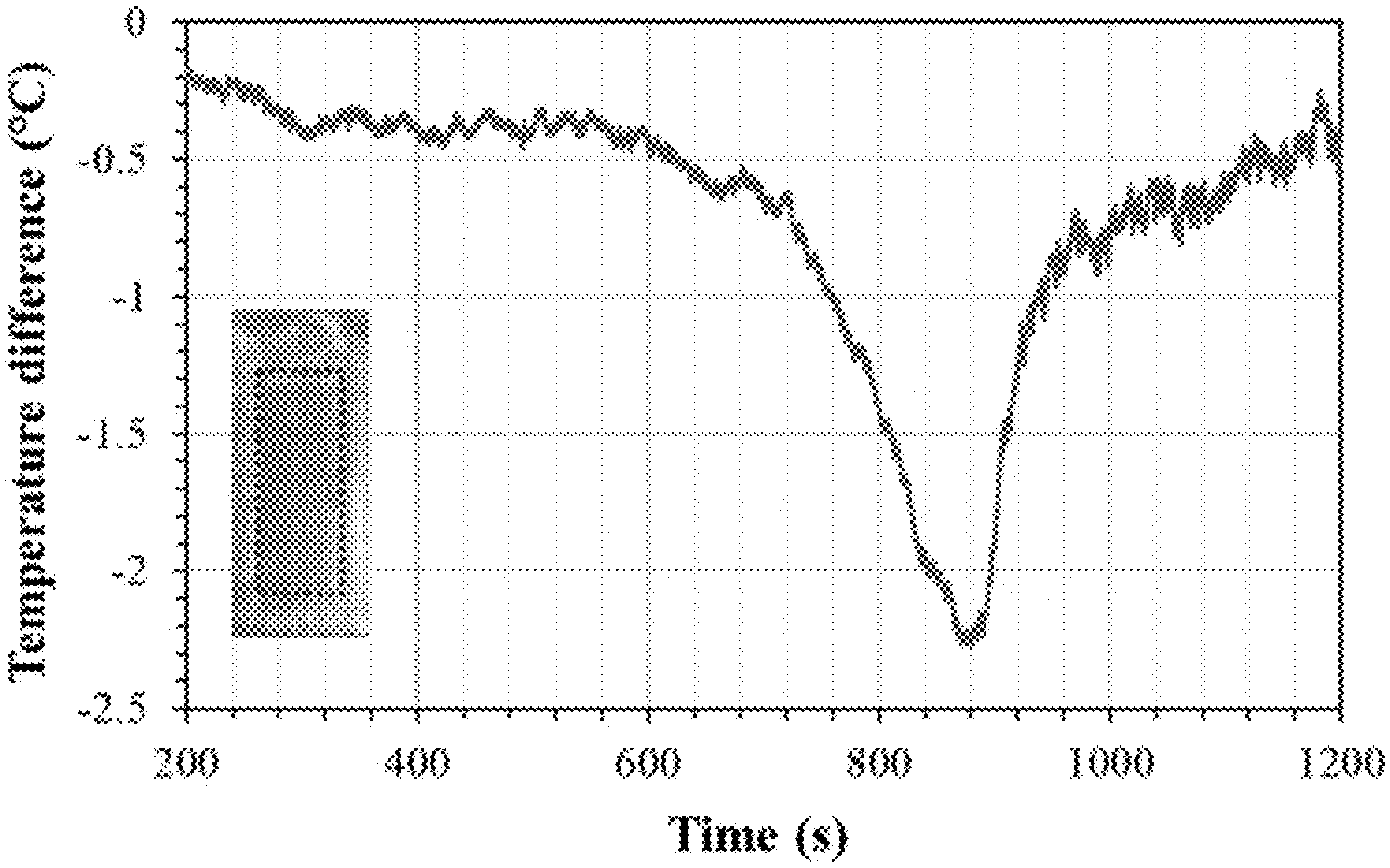

0
-0.5
-1
-1.5
-2
-2.5
Temperature difference (°C)
200
400
600
800
1000
1200
Time (s)

FIG. 7

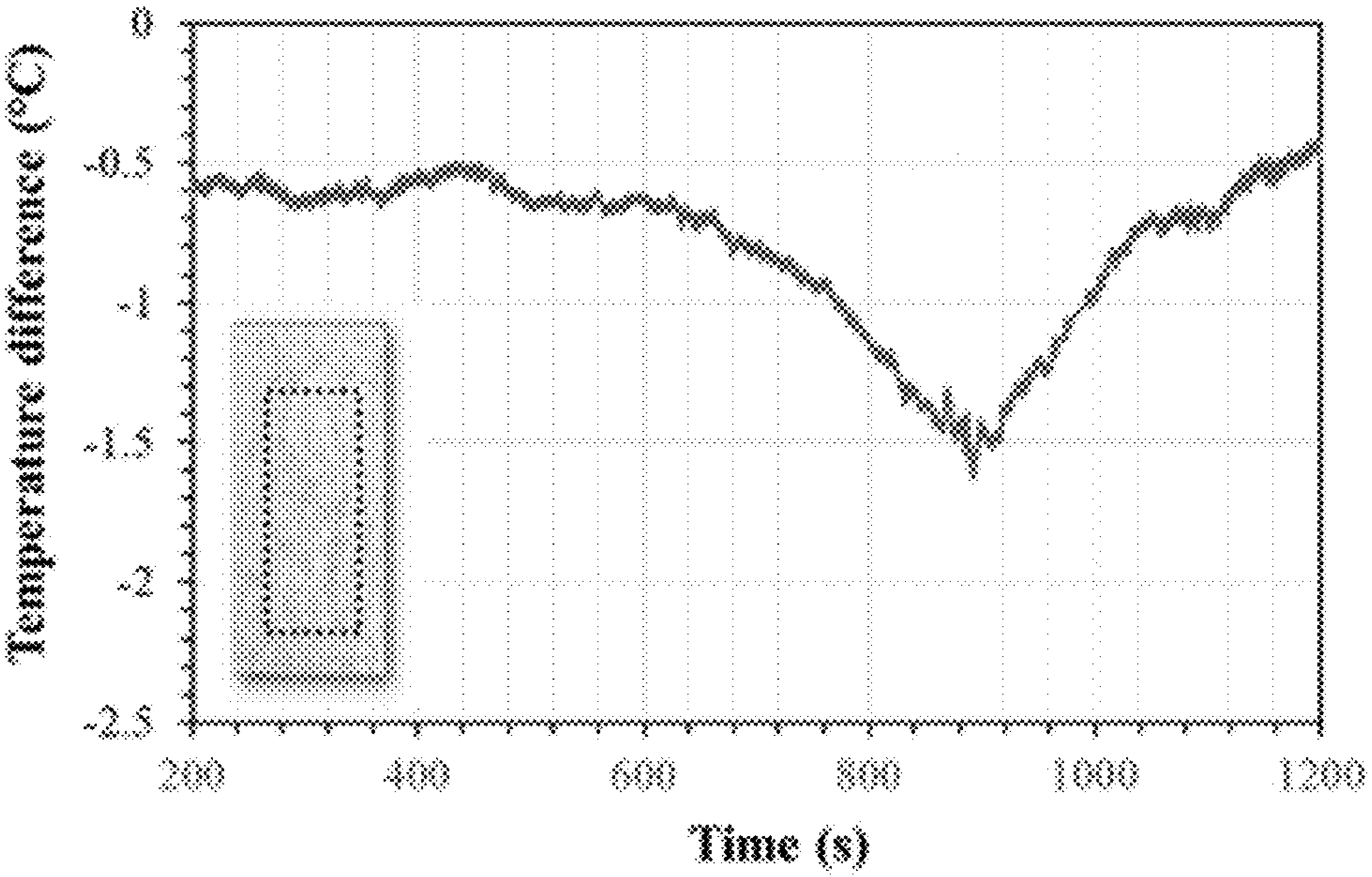

0
-0.5
-1
-1.5
-2
-2.5
Temperature difference (°C)
200
400
600
800
1000
1200
Time (s)

FIG. 8

MICROSTRUCTURAL SURFACE INCORPORATION OF PHASE CHANGE MATERIALS FOR THERMAL MANAGEMENT

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims priority to U.S. Provisional Patent Application Ser. No. 63/392,063, filed Jul. 25, 2022, which is incorporated by reference herein in its entirety.

BACKGROUND

[0002] Multiple systems and components operate at high power, high speed or under circumstances that expose them to elevated temperatures. All of these conditions could compromise the functionality of the systems and components. Thermal runaway in batteries, central processing unit (CPU) overheating, and ablation of materials are common examples of the negative effects that high temperatures can cause. To protect equipment from thermal damage, various types of thermal management systems have been developed, which can often be categorized into active and passive thermal management. Examples of active thermal management are refrigeration systems that pump refrigerant to absorb heat from one side of the system and expel heat at a different site. That is, the active thermal management system uses equipment to transport fluid that carries heat from the component to the environment. Such is the case on some refrigeration systems in DDG-51 class naval ships, which employ R-114 refrigerant. Overall, active thermal management strategies are a very effective means of reducing temperature in a system. However, active thermal management requires different designs and additional power compared to passive management approaches, resulting in higher operating costs. To cut down on energy costs, industries have been investing in passive cooling systems, which employ materials and/or geometries applied to equipment to effectively exchange heat with the environment without the need of a power source. Heat sinks, heat spreaders, and heat pipes are all examples of passive thermal management.

[0003] Phase change materials are another example of a passive thermal management approach. Phase change materials absorb and release heat at temperatures at or near their phase change temperature. These phase changes are endothermic while heating (when the material is transitioning from solid to liquid) and exothermic upon cooling (during the transformation from liquid back to solid). Furthermore, phase change materials have been successfully employed by diverse industries, from solar, buildings/construction, to textiles, and electronics.

BRIEF DESCRIPTION

[0004] A fabrication route capable of generating porous structures without damaging the host structure or reducing its mechanical properties is disclosed herein. The desired micro channels or pores accept a phase change material and be strong enough to sustain the various forces placed upon them. Moreover, the phase change materials will need to be sealed to prevent leakage during the heating stages and be able to sustain multiple thermal cycles.

[0005] The concept of generating a porous anodic layer on the surface of a metallic component to host a phase change material (phase change materials) is intended to reduce the peak temperatures that the host structure will experience.

[0006] Disclosed, in some embodiments, is a process for protecting an article from thermal damage. The process includes anodizing a metallic surface of the article to form an anodic layer comprising a metal oxide; annealing the anodic layer; introducing a phase change material to pores defined by the anodic layer; and applying a seal layer to seal the phase change material within the pores. The metallic surface may contain aluminum or an aluminum alloy. In some embodiments, the metallic surface is anodized with oxalic acid or sulfuric acid. The phase change material may contain n-eicosane. In some embodiments, the article is a heat sink, a casing, a fan, or a circuit board cooling device. Non-limiting examples of casings include a pump casing, a transmission casing, a differential casing, an electronics casing, and a power generation heat exchange casing.

[0007] Disclosed, in other embodiments, is an article including a metallic substrate; an anodic layer comprising a metal oxide formed on the metallic substrate and defining a plurality of pores; a phase change composition within the plurality of pores; and a seal layer sealing the phase change composition within the plurality of pores. The metallic substrate may contain aluminum or an aluminum alloy. In some embodiments, the phase change material includes n-eicosane. The article may be a heat sink.

[0008] Disclosed, in further embodiments, is a method for microstructural surface incorporation of phase change materials. The method includes anodizing a surface of an article including an aluminum alloy with an acid; annealing the aluminum alloy in air at a temperature below the melting point of the aluminum alloy; vacuum-impregnating the aluminum alloy with a phase change material; and applying a seal layer over the aluminum alloy and phase change material. The seal layer may include an epoxy resin or a silver paint. In some embodiments, the surface is anodized with oxalic acid or sulfuric acid. The phase change material may include n-eicosane.

[0009] These and other non-limiting characteristics are more particularly described below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] The following is a brief description of the drawings, which are presented for the purposes of illustrating the exemplary embodiments disclosed herein and not for the purposes of limiting the same.

[0011] FIG. **1** is a flow chart illustrating a method for producing a thermally protected article in accordance with some embodiments of the present disclosure.

[0012] FIG. **2** is a side cross-sectional view of a portion of a thermally protected composite in accordance with some embodiments of the present disclosure.

[0013] FIG. **3** includes SEM images of surface structures produced during a 40-minute anodization treatment at different acid concentrations and voltages as discussed in the Examples.

[0014] FIG. **4** includes SEM images of surface structures produced during a 25-minute anodization treatment at different acid concentrations and voltages as discussed in the Examples.

[0015] FIG. **5** includes pore size distribution graphs for different treatment lengths as discussed in the Examples.

[0016] FIG. **6** is a temperature profile graph as discussed in the Examples.

[0017] FIG. **7** is a temperature different graph for a specimen utilizing an epoxy sealant as discussed in the Examples.

[0018] FIG. **8** is a temperature different graph for a specimen utilizing a silver paint sealant as discussed in the Examples.

DETAILED DESCRIPTION

[0019] The present disclosure may be understood more readily by reference to the following detailed description of desired embodiments included therein, the drawings. In the following specification and the claims which follow, reference will be made to a number of terms which shall be defined to have the following meanings.

[0020] Unless otherwise defined, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art. In case of conflict, the present document, including definitions, will control. Preferred methods and materials are described below, although methods and materials similar or equivalent can be used in practice or testing of the present disclosure. All publications, patent applications, patents, and other references mentioned herein are incorporated by reference in their entirety. The materials, methods, and articles disclosed herein are illustrative only and not intended to be limiting.

[0021] The singular forms "a," "an," and "the" include plural referents unless the context clearly dictates otherwise.

[0022] As used in the specification and in the claims, the term "comprising" may include the embodiments "consisting of" and "consisting essentially of." The terms "comprise(s)," "include(s)," "having," "has," "can," "contain(s)," and variants thereof, as used herein, are intended to be open-ended transitional phrases that require the presence of the named ingredients/steps and permit the presence of other ingredients/steps. However, such description should be construed as also describing compositions, mixtures, or processes as "consisting of" and "consisting essentially of" the enumerated ingredients/steps, which allows the presence of only the named ingredients/steps, along with any impurities that might result therefrom, and excludes other ingredients/steps.

[0023] Unless indicated to the contrary, the numerical values in the specification should be understood to include numerical values which are the same when reduced to the same number of significant figures and numerical values which differ from the stated value by less than the experimental error of the conventional measurement technique of the type used to determine the particular value.

[0024] All ranges disclosed herein are inclusive of the recited endpoint and independently combinable (for example, the range of "from 2 to 10" is inclusive of the endpoints, 2 and 10, and all the intermediate values). The endpoints of the ranges and any values disclosed herein are not limited to the precise range or value; they are sufficiently imprecise to include values approximating these ranges and/or values.

[0025] As used herein, approximating language may be applied to modify any quantitative representation that may vary without resulting in a change in the basic function to which it is related. Accordingly, a value modified by a term or terms, such as "about" and "substantially," may not be limited to the precise value specified, in some cases. The modifier "about" should also be considered as disclosing the range defined by the absolute values of the two endpoints. For example, the expression "from about 2 to about 4" also discloses the range "from 2 to 4." The term "about" may refer to plus or minus 10% of the indicated number. For example, "about 10%" may indicate a range of 9% to 11%, and "about 1" may mean from 0.9-1.1.

[0026] For the recitation of numeric ranges herein, each intervening number there between with the same degree of precision is explicitly contemplated. For example, for the range of 6-9, the numbers 7 and 8 are contemplated in addition to 6 and 9, and for the range 6.0-7.0, the number 6.0, 6.1, 6.2, 6.3, 6.4, 6.5, 6.6, 6.7, 6.8, 6.9, and 7.0 are explicitly contemplated.

[0027] FIG. **1** is a flow chart illustrating a process **100** in accordance with some embodiments of the present disclosure. The process **100** includes pretreating a metal substrate **110**, anodizing the metal substrate **120**, annealing the metal substrate **130**, providing a phase change material to pores **140**, and applying a seal layer to seal in the phase change material **150**.

[0028] FIG. **2** is a side cross-sectional view of a portion of thermally protected component **201** in accordance with some embodiments of the present disclosure. The component **201** includes a metal substrate **215**, an oxide layer **225**, a phase change material **235** provided in a pore, and a seal layer **245**. Only one pore is illustrated. However, it should be understood that FIG. **2** illustrates only a portion of a component, and a plurality of pores will be present. Moreover, the depicted pore and other elements are not drawn to scale.

[0029] The metal substrate **215** may contain at least one metal element and/or at least one metalloid element. The metal(s) may be selected from Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Cn, Nh, Fl, Mc, and Lv. The metalloid(s) may be selected from B, Si, Ge, As, Sb, and Te.

[0030] In particular embodiments, the metal substrate **215** comprises elemental aluminum or an aluminum alloy.

[0031] The aluminum alloy may be a 1000 series aluminum alloy, a 2000 series aluminum alloy, a 3000 series aluminum alloy, a 4000 series aluminum alloy, a 5000 series aluminum alloy, a 6000 series aluminum alloy, a 7000 series aluminum alloy, an 8000 series aluminum alloy, or a 9000 series aluminum alloy.

[0032] The aluminum content in the aluminum alloy may be at least 50 wt %, at least wt %, at least 70 wt %, at least 80 wt %, at least 85 wt %, at least 90 wt %, at least 91 wt %, at least 92 wt %, at least 93 wt %, at least 94 wt %, at least 95 wt %, at least 96 wt %, at least 97 wt %, at least 98 wt %, or at least 99 wt %.

[0033] In addition to aluminum, the aluminum alloy may contain one or more metal or metalloid selected from the group consisting of Li, Be, Na, Mg, Al, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, Cs, Ba, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, Ta, W, Re, Os, Ir, Pt, Au, Hg, Tl, Pb, Bi, Po, Fr, Ra, Ac, Th, Pa, U, Np, Pu, Am, Cm, Bk, Cf, Es, Fm, Md, No, Lr, Rf, Db, Sg, Bh, Hs, Mt, Ds, Rg, Cn, Nh, Fl, Mc, Lv, B, Si, Ge, As, Sb, and Te.

[0034] The substrate **215** may have a thickness in the range of about 0.1 μm to about 900 μm, including from about 1 μm to about 800 μm and from about 10 μm to about 700 μm.

[0035] Pretreatment **110** of the substrate may include cleaning. Cleaning may utilize a sodium hydroxide solution in some embodiments. Although not specifically illustrated in FIG. **1**, it is also contemplated that cleaning may occur after one or more of the anodizing **120**, annealing **130**, phase change material introduction **140**, and/or seal layer application **150**. When more than one cleaning step is utilized, the steps may be different as it is known in the art that different surface compositions may require different treatments to remove contaminants. For example, after anodization **120**, the surface may be rinsed with deionized water, ethanol, and dried.

[0036] The anodization **120** may utilize an acid. The acid may be provided in a solution (e.g., an aqueous solution). Non-limiting examples of acids include sulfuric acid, oxalic acid, chromic acid, tartaric acid, citric acid, malic acid, boric acid, and phosphoric acid. Combinations of any two or more of the aforementioned acids may also be used.

[0037] The concentration of the acid may be in a range of about 0.1 M to about 5 M, including from about 0.5 M to about 2.5 M, and about 1.2 M to about 1.6 M.

[0038] The applied voltage during the anodization **120** may be in a range of about 10 V to about 150 V, including from about 20 V to about 100 V, and about 30 V to about 40 V.

[0039] Anodization **120** may be performed for a time period of from about 1 minute to about 90 minutes, including from about 5 minutes to about 60 minutes, and from about minutes to about 40 minutes.

[0040] Temperature during anodization **120** may be in a range of about 20° C. to about ° C., including from about 30° C. to about 50° C., and about 35° C. to about 45° C.

[0041] Anodization **130** may result in pore sizes (average or median) in a range of about 1 nm to about 500 nm, including from about 3 nm to about 200 nm, from about 4 nm to about 100 nm, and from about 5 nm to about 85 nm.

[0042] Annealing **130** is intended to improve the mechanical robustness prior to the introduction of the phase change material.

[0043] Annealing **130** may be conducted at a temperature in a range of from about 400° C. to about 600° C., including from about 450° C. to about 550° C., and about 475° C. to about 525° C.

[0044] In some embodiments, annealing **130** is performed for a time period of from about 10 minutes to about 210 minutes, including from about 30 minutes to about 180 minutes, and from about 90 minutes to about 150 minutes.

[0045] The annealed article may be permitted to cool after annealing **130**.

[0046] The phase change material may be introduced **140** via vacuum impregnation.

[0047] The phase change material **235** may be selected from waxes (e.g., paraffin wax), hydrocarbons (e.g., alkane hydrocarbons), fatty acids (e.g., stearic acid), hydrated salts, and phase change alloys such as indium-bismuth-tin alloys (e.g., Field's alloy which contains about 51% indium, about 32.5% bismuth, and about 16.5% tin. Mixtures and composites are also contemplated. Non-limiting examples of alkanes include any one or more of n-octacosane, n-heptacosane, n-hexacosane, n-pentacosane, n-tetracosane, n-docosane, n-tricosane, n-heneicosane, n-eicosane, n-nonadecane, n-octadecane, n-heptadecane, n-hexadecane, n-pentadecane, n-tetradecane, and n-tridecane.

[0048] The phase change material may be introduced along with one or more additives. Non-limiting examples of suitable additives include both nano-scale additives and/or micro-scale additives and, in some embodiments, may be selected from metals, metal oxides, and carbon-based materials (e.g., graphene, carbon nanotubes).

[0049] Non-limiting examples of sealant materials **245** include epoxies and metallic paints (e.g., silver paints). It is also contemplated that stainless steel may be utilized for the seal layer.

[0050] The seal layer **245** may have a thickness in a range of about 0.005 mm to about 1 mm, including from about 0.01 mm to about 0.05 mm and from about 0.013 mm to about 0.018 mm.

[0051] The objective of the inclusion of the phase change material(s) is to reduce the peak temperatures that are observed when the metallic part is subjected to transient thermal loads. The reduced cross section of the surface layer did not meaningfully impact the functionality of the metallic component nor negatively impacted its mechanical properties during testing. The process disclosed herein could be applied to geometrically complex metallic substrates without the need for design and fabrication modifications, which cannot be achieved by the procedures known in the art. The process can be applied as a post-processing step in complex metallic parts, and will minimally impact the existing design, weight, and overall mechanical properties.

[0052] The process could be applied to any metallic substrate that is subject to thermal loads and is required to stay within a certain temperature range for optimal performance. Potential applications include but are not limited to:

- **[0053]** high power electronics;
- **[0054]** micro-electronics;
- **[0055]** heating ventilating and air conditioning heat (HVAC) exchange systems;
- **[0056]** machinery casings to include pump, transmission, and differential casings;
- **[0057]** power generation heat exchange casings;
- **[0058]** 3D printer heat exchanger fans;
- **[0059]** electronics casings; and
- **[0060]** circuit board cooling devices.

[0061] The process results in the incorporation of phase change materials into a metallic part at the microstructural level through a simple postproduction process that could be applied to existing, geometrically complex components.

[0062] Some advantages of the approach presented herein are the simplicity of the strategy, the small amounts of phase change materials required, and that there is no need to redesign the components. Moreover, anodization is a widely employed surface treatment and the process is easily scalable. The mechanical properties of the original metallic part may remain unchanged or relatively unchanged.

[0063] The following examples are provided to illustrate the devices and methods of the present disclosure. The examples are merely illustrative and are not intended to limit the disclosure to the materials, conditions, or process parameters set forth therein.

Examples

[0064] The conditions to fabricate a porous anodic layer on top of an aluminum substrate were determined through varying anodization conditions: solution concentration, voltage employed and anodization times. Pore sizes were characterized using scanning electron microscopy. The alkane n-eicosane was selected as a phase change material, introduced within the porous anodic annealed layer using vacuum impregnation, and then the thin film composite structure was sealed. Epoxy resin and a metallic paste were tested as sealants. Thermal tests were performed to compare the behavior of aluminum alloy substrates anodized and sealed with and without phase change materials. The results showed that the aluminum alloy impregnated with n-eicosane presents lowered peak temperatures during heating cycles than the samples that were only anodized or than the base alloy, demonstrating the potential of phase change materials incorporated in the superficial microstructure of anodic structures to manage, to a certain extent, peak transient thermal loads.

[0065] An anodic layer was successfully fabricated on a given aluminum surface from an existing part. By adjusting the variables of electrolyte concentration, electrolyte temperature, time, and voltage, an anodic layer that contained pores with an average diameter of 50 nm were consistently fabricated for use with various phase change materials and sealant methods.

[0066] The anodic layer was then annealed, a step that increased the mechanical robustness of the layer. Vacuum impregnation was successfully employed to incorporate phase change materials into the porous anodic structure and sealed with various coating agents. The vacuum impregnation chamber constructed as part of this work was highly effective at creating a vacuum seal. The metal-phase change materials composite generated withstood multiple heating cycles during the vacuum impregnation process which was critical to the fabrication of multiple phase change materials incorporated anodic samples.

[0067] The results indicate that there is a reduction of 1 to 2.3° C. in the peak temperatures that the metallic host experiences, with only 0.05 grams of n-eicosane was spread throughout a 120 mm^2 section of aluminum, which is itself a remarkable result for a composite structure that only measures a few microns height and contains pores in the nanometer scale located in the surface of the component.

[0068] Materials and Methods

[0069] Surface Layer Fabrication

[0070] Instead of starting with the full body of a heat sink, these examples employed an aluminum fin that was removed from a commercial heat sink to serve as proof of concept that could later be scaled up. The aluminum fin was anodized to create a porous layer, annealed at moderate temperatures to strengthen the anodic structure, vacuum impregnated with n-eicosane phase change materials, and sealed with either epoxy resin or silver paste.

[0071] The aluminum alloy sample to be anodized was employed as the anode while the cropped aluminum heat sink base of the same alloy was used as a cathode. The cathode had a surface area that was significantly larger than that of the anode (1:32 ratio). Electrical insulation tape was used to cover the back and the edges of the aluminum fin anode, leaving approximately 120 mm^2 of aluminum exposed to the electrolyte. A DC power source (Model XLN15101 B&K Precision Corp, Yorba Linda, CA, US) and digital multimeter (Model 2100 Keithley Instruments, Cleveland, OH, US) were placed in series and connected to metal clamps that held the anode and cathode, the positive end being connected to the anode and the negative end to the cathode. The power source was programmed to supply a fixed amount of voltage over a set amount of time.

[0072] Concerning the anodization conditions, the method was adopted from a study conducted by Sanz et al. ("Aluminum Anodization in Oxalic Acid: Controlling the Texture of Al_2O_3/Al Monoliths for Catalytic Applications," *Ind. Eng. Chem. Res.*, vol. 50, no. 4, pp. 2117-2125, Feb. 2011, DOI: 10.1021/ie102122x which is incorporated by reference herein in its entirety). For the purposes of this study, well-structured open pores of micrometer scale length were sought after to host the phase change materials. The aluminum was anodized at 1.2 and 1.6 M oxalic acid (98%, Sigma-Aldrich, Burlington, MA, US) concentrations, using voltages of 20, 30, 40 and 100 V, with a fixed value of 40° C. for the bath temperature. The experiments were performed during time intervals that spanned between 10 and 40 minutes.

[0073] After the creation of the anodic layer, the tape employed to limit the area exposed to the bath was removed from the fin samples, which were then rinsed with DI water, ethanol and dried. The specimens were placed in an oven at 500° C. for 2 hours (process herein referred as anneal) and allowed to gradually cool.

[0074] During the vacuum impregnation process, the non-anodic sections of the aluminum fin were again covered in tape, and 0.05 g of solid n-Eicosane (Millipore Sigma, Saint Louis, MO, US) was placed on top of the anodic layer. The fin was then placed in a hermetically sealed dish that was connected to a vacuum pump (roughing pump that achieves 1×10^{-3} torr) and placed into a binder convection oven (Binder GmbH, Tuttlingen, Germany). Once the vacuum pump was activated, the oven was set to 45° C. for the phase change materials to melt. The intent of placing the liquid phase change materials below atmospheric pressure was to force the phase change materials to fill the vertically oriented pores that the anodization step produced. Samples were allowed to cool while under vacuum.

[0075] To prevent phase change material leakage during the heating and cooling cycles, each sample was sealed by the application of a surface coat. Diverse sealing materials were compared based on their availability, ease of application, thermal stability, and on the ability to contain the phase change materials after several heating cycles. To prepare each sample, the outer rim of the aluminum fin was washed with ethanol to ensure that all tape residue from the vacuum impregnation process had been removed. The non-anodic surface was then sanded with 300 grit sandpaper to ensure that the chosen sealant had a strong mechanical bond to the area surrounding the phase change material.

[0076] Epoxy resin was used as one of the methods of encapsulation. Epofix resin (Struers, Ballerup, Denmark), with a 25 to 3 resin to hardener ratio by mass, was chosen for the first experiment. The resin-hardener mixture was stirred for five minutes and allowed to settle for five additional minutes. Then a thin coat of epoxy was applied with a fine haired brush. Once the fin had the uncured epoxy applied, it was placed in the same vacuum chamber used for impregnation to remove air bubbles introduced from mixing the epoxy components. Once the vacuum was applied using the roughing pump, the epoxy system was allowed to dry at room temperature for 24 hours.

[0077] The second sealant used, here referred to as silver paint, was composed of silver particles dispersed in Iso-Butyl Methyl Ketone (Ted Pella Inc. Redding, CA, US). To distribute the silver particles prior to application, the silver paint bottle was placed in an ultrasonic cleaner for ten minutes. After covering the fin with silver paint, the aluminum fin was placed in the vacuum chamber for thirty minutes. While the aluminum fin was drying in the vacuum chamber, the silver paint was placed in the sonication bath to ensure that any particles displaced after the first application were again evenly distributed. After thirty minutes, a second coat of silver paint was applied to the entire surface and placed in the vacuum chamber for thirty minutes, after which the vacuum pump was turned off and the fin was left to dry for 24 hours.

[0078] The porous structures produced were observed employing scanning electron microscopy (SEM). A Zeiss Neon **40** (Carl Zeiss Inc., Thornwood, NY, USA) field emission SEM and a FEI Inspect 50 SEM (Field Electron and Ion Company, Hillboro, OR, US), both operating between 1 and 20 KV were used to characterize the pore sizes and anodic layer height. The software program Image J (National Institutes of Health, Bethesda, Maryland, US) was used for the statistical analysis of pore sizes.

[0079] Once the phase change material was sealed, thermal testing was conducted using a FLIR USETS320 thermal camera (FLIR Systems Inc. San Carlos, CA, US). The thermal test was constructed by placing a Pyrex dish filled with sand on top of a hot plate and positioning the samples on top of the sand. The FLIR camera was set 65 mm above the samples surface. The sand bed was used to slow the heating rate, allowing the measurement of the local temperatures within each sample. A bare aluminum fin, along anodized-annealed-sealed fins with, and without phase change materials, were tested simultaneously. The samples were sealed under identical conditions to match their emissivity. Heating and cooling cycles were run, and the temperature plotted with respect to time for each sample.

[0080] Visual observation of the fin samples showed a yellow deposit after anodization, which turned brown after thermal treatments at 500° C. The melting and dispersion of the phase change materials during vacuum impregnation left a thin film that was later coated. The silver sealant was observed for the specimen utilizing silver paint. Other specimens showed a transparent coat (epoxy resin) that allowed the observation of the underlying structure.

[0081] The pores generated by diverse anodization conditions are presented in FIGS. **3** and **4**. Those SEM images show evidence of regular arrangement of pores under most conditions employed. All samples in FIG. **3** were fabricated by experiments that lasted 40 min at 40° C. in their respective concentrations. Larger pore volumes are observed for samples generated at 40 V when compared to those produced at 20 or 30 V. When looking at the oxalic acid concentration of 1.6 M, it was observed that higher voltages created larger diameter pore sizes in the anodic structure. For the application of phase change material impregnation, these larger pore sizes were preferred. Since the largest pore size shown in FIG. **3** is observed at 40 V, such voltage and concentration were chosen to move forward with for the anodic layer development.

[0082] With the voltage and concentration of the solution fixed at 40 V and 1.6 M respectively, time would not only determine the thickness of the anodic layer, but also the pore morphology. FIG. **4** details the effects of anodization times: after 25 min under the mentioned experimental conditions, a more disordered and misoriented group of pores is generated. With an increase in porosity comes a thinning of the cell walls that surround each anodic pore, increasing the likelihood of columns that bend and break, blocking the anodic pores and rendering a microstructure ineffective for phase change materials impregnation and reduced ability to hold the phase change materials during thermal cycling.

[0083] A more detailed analysis of the effects of time in the pore size distribution is presented in FIG. **5**, where it can be observed that most pores have diameters in the 5-85 nm range, with average values that increase as the time of anodization is extended.

[0084] Comparing these results with studies done in the past with anodic structures produced with oxalic acid, it is clear that there is a point in which overgrowth could occur. As temperature, current density, and electrolyte concentration increase, the rate at which the pores form increases. As time continues to advance, the formation of the anodic layer becomes thicker, while the diameters of the pores will continue to grow larger. Those pores will eventually experience overgrowth or chalking. Chalking is due to a chemical attack at the outer part of the oxide film which thins the pore walls and causes their upper regions to lose structural stability and collapse.

[0085] Thermal treatment at 500° C. did not cause significant changes in the microstructure of the samples, or in morphology and size since SEM observations rendered diameters within the standard deviation of the measurements taken before annealing. The vacuum impregnation of the phase change materials in the anodic structures was followed by the application of a surface coat.

[0086] FIG. **6** shows the temperature profiles of samples tested with and without phase change materials. The phase change experienced by the phase change materials produced the expected endothermic reaction during phase change materials melting (M.P. 36-38° C.), and an exothermic reaction during solidification. Upon heating, this endothermic reaction slowed the rate of heating a significant amount. This effect lasted for approximately 4.88 minutes starting at a temperature of 37.06° C. and ending at a temperature of 39.02° C. This resulted in a maximum temperature difference of 2.27° C. when compared with the anodic layer with an epoxy coat and no phase change materials, and a maximum temperature difference of 1° C. when compared with raw aluminum. Upon cooling, the exothermic reaction peaked at 36.96° C., which is below the lower bounds of the phase change materials liquid phase transition temperature. During testing, however, the phase change materials leaked out of the epoxy coating, reducing the effectiveness of the sample to withstand repeated cycles.

[0087] The test performed with phase change materials sealed with two thin coats of silver paint presented a similar cooling effect than the one observed with Epofix. However, the silver paint coating was able to contain the phase change materials upon heating and cooling, a promising result regarding repeatability. The maximum relative temperature difference 1.63° C. when compared with the anodic layer with the silver coat and no phase change materials, and a maximum temperature difference of 3.35° C. when compared with raw aluminum.

[0088] FIGS. **7** and **8** are graphs showing the temperature differences between metallic samples that had an anodic structure that was annealed and sealed and one that had the annealed anodic structure containing phase change materials and sealed with Epofix coat (FIG. **7**) or silver paint coat (FIG. **8**) along with the images of the respective samples. Larger differences between the samples with and without phase change materials are detected for samples sealed with epoxy resin than those sealed with silver paint, although the latter seems to maintain the lower temperature during longer periods of time.

[0089] Other literature that encapsulates phase change materials in heat spreaders or similar structures reports larger reductions in peak temperatures than those observed here. However, in those cases, the metallic component employed had to be redesigned to host the phase change materials. From the observed results, it can be said that greater distribution of phase change materials with a conductor's surface area allows the phase change materials to efficiently absorb heat from the conductor resulting in a net reduction of surface temperatures between 1 and 2.3° C. with only 0.05 grams of n-eicosane was spread throughout a 120 mm^2 section of aluminum. Phase change materials within the anodic layer containing features in the nanometer scale increased the surface area contact of the phase change materials-conductor interface. As a proof of concept, these examples proved that the efficient application of the phase change materials within the microstructure can decrease the peak transient thermal loads of the system into which the phase change material is integrated. Given the results presented herein, it is believed that latent heat energy storage could be achieved in more compact passive heat management devices, paving the way for technological advancement in the field of thermal management. Furthermore, phase change materials incorporated within the surface microstructure of components could be applied not only to electronic devices, but to machinery and other systems that operate under cyclic loads.

[0090] This written description uses examples to describe the disclosure, including the best mode, and also to enable any person skilled in the art to make and use the disclosure. Other examples that occur to those skilled in the art are intended to be within the scope of the present disclosure if they have structural elements that do not differ from the same concept, or if they include equivalent structural elements with insubstantial differences. It will be appreciated that variants of the above-disclosed and other features and functions, or alternatives thereof, may be combined into many other different systems or applications. Various presently unforeseen or unanticipated alternatives, modifications, variations, or improvements therein may be subsequently made by those skilled in the art which are also intended to be encompassed by the following claims.

1. A process for protecting an article from thermal damage, the process comprising in sequence:
   anodizing a metallic surface of the article to form an anodic layer comprising a metal oxide;
   annealing the anodic layer;
   introducing a phase change material to pores defined by the anodic layer; and
   applying a seal layer to seal the phase change material within the pores.

2. The process of claim **1**, wherein the metallic surface comprises aluminum.

3. The process of claim **1**, wherein the metallic surface comprises an aluminum alloy.

4. The process of claim **1**, wherein the metallic surface is anodized with oxalic acid.

5. The process of claim **1**, wherein the metallic surface is anodized with sulfuric acid.

6. The process of claim **1**, wherein the phase change material comprises n-eicosane.

7. The process of claim **1**, wherein the article comprises a heat sink.

8. The process of claim **1**, wherein the article comprises a casing, a fan, or a circuit board cooling device.

9. The process of claim **8**, wherein the casing is selected from the group consisting of a pump casing, a transmission casing, a differential casing, an electronics casing, and a power generation heat exchange casing.

10. An article comprising:
    a metallic substrate;
    an anodic layer comprising a metal oxide formed on the metallic substrate and defining a plurality of pores;
    a phase change composition within the plurality of pores; and
    a seal layer sealing the phase change composition within the plurality of pores.

11. The article of claim **10**, wherein the metallic substrate comprises aluminum.

12. The article of claim **10**, wherein the metallic substrate comprises an aluminum alloy.

13. The article of claim **10**, wherein the phase change material comprises n-eicosane.

14. The article of claim **10**, wherein the article comprises a heat sink.

15. A method for microstructural surface incorporation of phase change materials, the method comprising:
    anodizing a surface of an article comprising an aluminum alloy with an acid;
    annealing the aluminum alloy in air at a temperature below the melting point of the aluminum alloy;
    vacuum-impregnating the aluminum alloy with a phase change material; and
    applying a seal layer over the aluminum alloy and phase change material.

16. The method of claim **15**, wherein the seal layer comprises an epoxy resin.

17. The method of claim **15**, wherein the seal layer comprises silver paint.

18. The method of claim **15**, wherein the surface is anodized with oxalic acid.

19. The method of claim **15**, wherein the surface is anodized with sulfuric acid.

20. The method of claim **15**, wherein the phase change material comprises n-eicosane.

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