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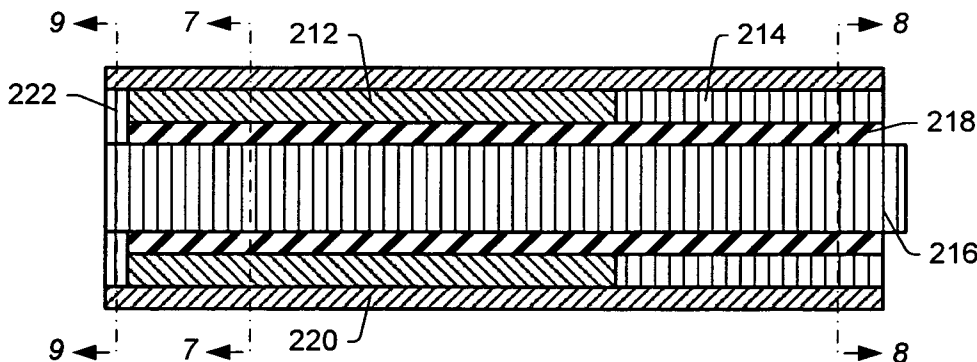
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(54) Title: ADJUSTING ALLOY COMPOSITIONS FOR SELECTED PROPERTIES IN TEMPERATURE LIMITED HEATERS



(57) Abstract: A heater is described. The heater includes a heater section including iron, cobalt, and carbon. The heater section has a Curie temperature less than a phase transformation temperature. The Curie temperature is at least 740 °C. The heater section provides, when time varying current is applied to the heater section, an electrical resistance.

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ADJUSTING ALLOY COMPOSITIONS FOR SELECTED PROPERTIES IN  
TEMPERATURE LIMITED HEATERS

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**GOVERNMENT INTEREST**

The U.S. Government has certain rights in this invention pursuant to Agreement No. ERD-05-2516 between UT-Battelle, LLC, operating under prime contract No. DE-ACO5-00OR22725 for the US Department of Energy and Shell Exploration and Production Company.

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**BACKGROUND**

1. Field of the Invention

The present invention relates generally to heaters with temperature limiting properties. Specific embodiments relate to heaters used in the treatment of subsurface formations, such as hydrocarbon containing formations, to produce hydrocarbons, hydrogen, and/or other products from the formations.

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2. Description of Related Art

Hydrocarbons obtained from subterranean formations are often used as energy resources, as feedstocks, and as consumer products. Concerns over depletion of available hydrocarbon resources and concerns over declining overall quality of produced hydrocarbons have led to development of processes for more efficient recovery, processing and/or use of available hydrocarbon resources. In situ processes may be used to remove hydrocarbon materials from subterranean formations. Chemical and/or physical properties of hydrocarbon material in a subterranean formation may need to be changed to allow hydrocarbon material to be more easily removed from the subterranean formation. The chemical and physical changes may include in situ reactions that produce removable fluids, composition changes, solubility changes, density changes, phase changes, and/or viscosity changes of the hydrocarbon material in the formation. A fluid may be, but is not limited to, a gas, a liquid, an emulsion, a slurry, and/or a stream of solid particles that has flow characteristics similar to liquid flow.

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Heaters may be placed in wellbores to heat a formation during an in situ process. Examples of in situ processes utilizing downhole heaters are illustrated in U.S. Patent Nos. 2,634,961 to Ljungstrom; 2,732,195 to Ljungstrom; 2,780,450 to Ljungstrom; 2,789,805 to Ljungstrom; 2,923,535 to Ljungstrom; and 4,886,118 to Van Meurs et al.

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Application of heat to oil shale formations is described in U.S. Patent Nos. 2,923,535 to Ljungstrom and 4,886,118 to Van Meurs et al. Heat may be applied to the oil shale formation to pyrolyze kerogen in the oil shale formation. The heat may also fracture the formation to increase

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permeability of the formation. The increased permeability may allow formation fluid to travel to a production well where the fluid is removed from the oil shale formation. In some processes disclosed by Ljungstrom, for example, an oxygen containing gaseous medium is introduced to a permeable stratum, preferably while still hot from a preheating step, to initiate combustion.

5 A heat source may be used to heat a subterranean formation. Electric heaters may be used to heat the subterranean formation by radiation and/or conduction. An electric heater may resistively heat an element. U.S. Patent No. 2,548,360 to Germain describes an electric heating element placed in a viscous oil in a wellbore. The heater element heats and thins the oil to allow the oil to be pumped from the wellbore. U.S. Patent No. 4,716,960 to Eastlund et al. describes  
10 electrically heating tubing of a petroleum well by passing a relatively low voltage current through the tubing to prevent formation of solids. U.S. Patent No. 5,065,818 to Van Egmond describes an electric heating element that is cemented into a well borehole without a casing surrounding the heating element.

U.S. Patent No. 6,023,554 to Vinegar et al. describes an electric heating element that is  
15 positioned in a casing. The heating element generates radiant energy that heats the casing. A granular solid fill material may be placed between the casing and the formation. The casing may conductively heat the fill material, which in turn conductively heats the formation.

Some heaters may break down or fail due to hot spots in the formation. The power supplied to the entire heater may need to be reduced if a temperature along any point of the heater  
20 exceeds, or is about to exceed, a maximum operating temperature of the heater to avoid failure of the heater and/or overheating of the formation at or near hot spots in the formation. Some heaters may not provide uniform heat along a length of the heater until the heater reaches a certain temperature limit. Some heaters may not heat a subsurface formation efficiently. Some commonly used ferromagnetic metals found in heaters may have a phase transformation temperature that is  
25 below or overlaps a Curie temperature of the metal. Thus, it is advantageous to use ferromagnetic metal alloys that have metal compositions that adjust the phase transformation temperature of the alloy so that the Curie temperature is below a range of the phase transformation temperature.

#### **SUMMARY**

Embodiments described herein generally relate to systems, methods, and heaters for  
30 treating a subsurface formation. Embodiments described herein also generally relate to heaters that have novel components therein. Such heaters can be obtained by using the systems and methods described herein.

In certain embodiments, the invention provides one or more systems, methods, and/or heaters. In some embodiments, the systems, methods, and/or heaters are used for treating a  
35 subsurface formation.

In certain embodiments, the invention provides a heater, comprising: a heater section comprising iron, cobalt, and carbon; wherein the heater section has a Curie temperature ( $T_c$ ) less than a phase transformation temperature, and the  $T_c$  is at least 740 °C; and wherein the heater section is configured to provide, when time varying current is applied to the heater section, an electrical resistance.

In some embodiments, the invention provides the heater section having at most 1% by weight of manganese, at most 1% by weight of nickel, at most 1% by weight of silicon, at most 1% by weight of vanadium, at most 1% by weight of titanium, and/or at most 1% by weight of manganese.

In some embodiments, the invention provides the heater section having a Curie temperature ( $T_c$ ) less than a phase transformation temperature, and the  $T_c$  is at least 800 °C.

In some embodiments, the invention provides the heater section having at least 50% by weight iron, at least 9% by weight chromium and at least 0.1% by weight carbon.

In further embodiments, features from specific embodiments may be combined with features from other embodiments. For example, features from one embodiment may be combined with features from any of the other embodiments.

In further embodiments, treating a subsurface formation is performed using any of the methods, systems, or heaters described herein.

In further embodiments, additional features may be added to the specific embodiments described herein.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Advantages of the present invention may become apparent to those skilled in the art with the benefit of the following detailed description and upon reference to the accompanying drawings in which:

FIG. 1 depicts an illustration of stages of heating a hydrocarbon containing formation.

FIG. 2 shows a schematic view of an embodiment of a portion of an in situ heat treatment system for treating a hydrocarbon containing formation.

FIGS. 3, 4, and 5 depict cross-sectional representations of an embodiment of a temperature limited heater with an outer conductor having a ferromagnetic section and a non-ferromagnetic section.

FIGS. 6, 7, 8, and 9 depict cross-sectional representations of an embodiment of a temperature limited heater with an outer conductor having a ferromagnetic section and a non-ferromagnetic section placed inside a sheath.

FIG. 10 depicts an embodiment of a temperature limited heater in which the support member provides a majority of the heat output below the Curie temperature of the ferromagnetic conductor.

FIGS. 11 and 12 depict embodiments of temperature limited heaters in which the jacket provides a majority of the heat output below the Curie temperature of the ferromagnetic conductor.

FIG. 13 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for iron alloy TC3.

FIG. 14 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for iron alloy FM-4.

5 FIG. 15 depicts the Curie temperature and phase transformation temperature range for several iron alloys.

FIG. 16 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for an iron-cobalt alloy with 5.63% by weight cobalt and 0.4% by weight manganese.

10 FIG. 17 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for an iron-cobalt alloy with 5.63% by weight cobalt, 0.4% by weight manganese, and 0.01% carbon.

FIG. 18 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for an iron-cobalt alloy with 5.63% by weight cobalt, 0.4% by weight manganese, and 0.085% carbon.

15 FIG. 19 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for an iron-cobalt alloy with 5.63% by weight cobalt, 0.4% by weight manganese, 0.085% carbon, and 0.4% titanium.

FIG. 20 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for an iron-chromium alloys having 12.25% by weight chromium, 0.1% by weight carbon, 0.5% by weight manganese, and 0.5% by weight silicon.

While the invention is susceptible to various modifications and alternative forms, specific embodiments thereof are shown by way of example in the drawings and may herein be described in detail. The drawings may not be to scale. It should be understood, however, that the drawings and detailed description thereto are not intended to limit the invention to the particular form disclosed, but on the contrary, the intention is to cover all modifications, equivalents and alternatives falling within the spirit and scope of the present invention as defined by the appended claims.

#### **DETAILED DESCRIPTION**

The following description generally relates to systems and methods for treating hydrocarbons in the formations. Such formations may be treated to yield hydrocarbon products, hydrogen, and other products.

“Alternating current (AC)” refers to a time-varying current that reverses direction substantially sinusoidally. AC produces skin effect electricity flow in a ferromagnetic conductor.

In the context of reduced heat output heating systems, apparatus, and methods, the term “automatically” means such systems, apparatus, and methods function in a certain way without the

use of external control (for example, external controllers such as a controller with a temperature sensor and a feedback loop, PID controller, or predictive controller).

“Curie temperature” is the temperature above which a ferromagnetic material loses all of its ferromagnetic properties. In addition to losing all of its ferromagnetic properties above the  
5 Curie temperature, the ferromagnetic material begins to lose its ferromagnetic properties when an increasing electrical current is passed through the ferromagnetic material.

A “formation” includes one or more hydrocarbon containing layers, one or more non-hydrocarbon layers, an overburden, and/or an underburden. “Hydrocarbon layers” refer to layers in the formation that contain hydrocarbons. The hydrocarbon layers may contain non-hydrocarbon  
10 material and hydrocarbon material. The “overburden” and/or the “underburden” include one or more different types of impermeable materials. For example, the overburden and/or underburden may include rock, shale, mudstone, or wet/tight carbonate. In some embodiments of in situ heat treatment processes, the overburden and/or the underburden may include a hydrocarbon containing layer or hydrocarbon containing layers that are relatively impermeable and are not subjected to  
15 temperatures during in situ heat treatment processing that result in significant characteristic changes of the hydrocarbon containing layers of the overburden and/or the underburden. For example, the underburden may contain shale or mudstone, but the underburden is not allowed to heat to pyrolysis temperatures during the in situ heat treatment process. In some cases, the overburden and/or the underburden may be somewhat permeable.

20 “Formation fluids” refer to fluids present in a formation and may include pyrolyzation fluid, synthesis gas, mobilized hydrocarbon, and water (steam). Formation fluids may include hydrocarbon fluids as well as non-hydrocarbon fluids. The term “mobilized fluid” refers to fluids in a hydrocarbon containing formation that are able to flow as a result of thermal treatment of the formation. “Produced fluids” refer to fluids removed from the formation.

25 A “heat source” is any system for providing heat to at least a portion of a formation substantially by conductive and/or radiative heat transfer. For example, a heat source may include electric heaters such as an insulated conductor, an elongated member, and/or a conductor disposed in a conduit. A heat source may also include systems that generate heat by burning a fuel external to or in a formation. The systems may be surface burners, downhole gas burners, flameless  
30 distributed combustors, and natural distributed combustors. In some embodiments, heat provided to or generated in one or more heat sources may be supplied by other sources of energy. The other sources of energy may directly heat a formation, or the energy may be applied to a transfer medium that directly or indirectly heats the formation. It is to be understood that one or more heat sources that are applying heat to a formation may use different sources of energy. Thus, for example, for a  
35 given formation some heat sources may supply heat from electric resistance heaters, some heat sources may provide heat from combustion, and some heat sources may provide heat from one or

more other energy sources (for example, chemical reactions, solar energy, wind energy, biomass, or other sources of renewable energy). A chemical reaction may include an exothermic reaction (for example, an oxidation reaction). A heat source may also include a heater that provides heat to a zone proximate and/or surrounding a heating location such as a heater well.

5 A "heater" is any system or heat source for generating heat in a well or a near wellbore region. Heaters may be, but are not limited to, electric heaters, burners, combustors that react with material in or produced from a formation, and/or combinations thereof.

"Hydrocarbons" are generally defined as molecules formed primarily by carbon and hydrogen atoms. Hydrocarbons may also include other elements such as, but not limited to,  
10 halogens, metallic elements, nitrogen, oxygen, and/or sulfur. Hydrocarbons may be, but are not limited to, kerogen, bitumen, pyrobitumen, oils, natural mineral waxes, and asphaltites. Hydrocarbons may be located in or adjacent to mineral matrices in the earth. Matrices may include, but are not limited to, sedimentary rock, sands, silicilytes, carbonates, diatomites, and other porous media. "Hydrocarbon fluids" are fluids that include hydrocarbons. Hydrocarbon fluids  
15 may include, entrain, or be entrained in non-hydrocarbon fluids such as hydrogen, nitrogen, carbon monoxide, carbon dioxide, hydrogen sulfide, water, and ammonia.

An "in situ conversion process" refers to a process of heating a hydrocarbon containing formation from heat sources to raise the temperature of at least a portion of the formation above a pyrolysis temperature so that pyrolyzation fluid is produced in the formation.

20 An "in situ heat treatment process" refers to a process of heating a hydrocarbon containing formation with heat sources to raise the temperature of at least a portion of the formation above a temperature that results in mobilized fluid, visbreaking, and/or pyrolysis of hydrocarbon containing material so that mobilized fluids, visbroken fluids, and/or pyrolyzation fluids are produced in the formation.

25 "Insulated conductor" refers to any elongated material that is able to conduct electricity and that is covered, in whole or in part, by an electrically insulating material.

"Pyrolysis" is the breaking of chemical bonds due to the application of heat. For example, pyrolysis may include transforming a compound into one or more other substances by heat alone. Heat may be transferred to a section of the formation to cause pyrolysis.

30 "Pyrolyzation fluids" or "pyrolysis products" refers to fluid produced substantially during pyrolysis of hydrocarbons. Fluid produced by pyrolysis reactions may mix with other fluids in a formation. The mixture would be considered pyrolyzation fluid or pyrolyzation product. As used herein, "pyrolysis zone" refers to a volume of a formation (for example, a relatively permeable formation such as a tar sands formation) that is reacted or reacting to form a pyrolyzation fluid.

“Time-varying current” refers to electrical current that produces skin effect electricity flow in a ferromagnetic conductor and has a magnitude that varies with time. Time-varying current includes both alternating current (AC) and modulated direct current (DC).

The term “wellbore” refers to a hole in a formation made by drilling or insertion of a conduit into the formation. A wellbore may have a substantially circular cross section, or another cross-sectional shape. As used herein, the terms “well” and “opening,” when referring to an opening in the formation may be used interchangeably with the term “wellbore.”

Hydrocarbons in formations may be treated in various ways to produce many different products. In certain embodiments, hydrocarbons in formations are treated in stages. FIG. 1 depicts an illustration of stages of heating the hydrocarbon containing formation. FIG. 1 also depicts an example of yield (“Y”) in barrels of oil equivalent per ton (y axis) of formation fluids from the formation versus temperature (“T”) of the heated formation in degrees Celsius (x axis).

Desorption of methane and vaporization of water occurs during stage 1 heating. Heating of the formation through stage 1 may be performed as quickly as possible. For example, when the hydrocarbon containing formation is initially heated, hydrocarbons in the formation desorb adsorbed methane. The desorbed methane may be produced from the formation. If the hydrocarbon containing formation is heated further, water in the hydrocarbon containing formation is vaporized. Water may occupy, in some hydrocarbon containing formations, between 10% and 50% of the pore volume in the formation. In other formations, water occupies larger or smaller portions of the pore volume. Water typically is vaporized in a formation between 160 °C and 285 °C at pressures of 600 kPa absolute to 7000 kPa absolute. In some embodiments, the vaporized water produces wettability changes in the formation and/or increased formation pressure. The wettability changes and/or increased pressure may affect pyrolysis reactions or other reactions in the formation. In certain embodiments, the vaporized water is produced from the formation. In other embodiments, the vaporized water is used for steam extraction and/or distillation in the formation or outside the formation. Removing the water from and increasing the pore volume in the formation increases the storage space for hydrocarbons in the pore volume.

In certain embodiments, after stage 1 heating, the formation is heated further, such that a temperature in the formation reaches (at least) an initial pyrolyzation temperature (such as a temperature at the lower end of the temperature range shown as stage 2). Hydrocarbons in the formation may be pyrolyzed throughout stage 2. A pyrolysis temperature range varies depending on the types of hydrocarbons in the formation. The pyrolysis temperature range may include temperatures between 250 °C and 900 °C. The pyrolysis temperature range for producing desired products may extend through only a portion of the total pyrolysis temperature range. In some embodiments, the pyrolysis temperature range for producing desired products may include temperatures between 250 °C and 400 °C or temperatures between 270 °C and 350 °C. If a



temperature of hydrocarbons in the formation is slowly raised through the temperature range from 250 °C to 400 °C, production of pyrolysis products may be substantially complete when the temperature approaches 400 °C. Average temperature of the hydrocarbons may be raised at a rate of less than 5 °C per day, less than 2 °C per day, less than 1 °C per day, or less than 0.5 °C per day through the pyrolysis temperature range for producing desired products. Heating the hydrocarbon containing formation with a plurality of heat sources may establish thermal gradients around the heat sources that slowly raise the temperature of hydrocarbons in the formation through the pyrolysis temperature range.

The rate of temperature increase through the pyrolysis temperature range for desired products may affect the quality and quantity of the formation fluids produced from the hydrocarbon containing formation. Raising the temperature slowly through the pyrolysis temperature range for desired products may inhibit mobilization of large chain molecules in the formation. Raising the temperature slowly through the pyrolysis temperature range for desired products may limit reactions between mobilized hydrocarbons that produce undesired products. Slowly raising the temperature of the formation through the pyrolysis temperature range for desired products may allow for the production of high quality, high API gravity hydrocarbons from the formation. Slowly raising the temperature of the formation through the pyrolysis temperature range for desired products may allow for the removal of a large amount of the hydrocarbons present in the formation as hydrocarbon product.

In some in situ heat treatment embodiments, a portion of the formation is heated to a desired temperature instead of slowly heating the temperature through a temperature range. In some embodiments, the desired temperature is 300 °C, 325 °C, or 350 °C. Other temperatures may be selected as the desired temperature. Superposition of heat from heat sources allows the desired temperature to be relatively quickly and efficiently established in the formation. Energy input into the formation from the heat sources may be adjusted to maintain the temperature in the formation substantially at the desired temperature. The heated portion of the formation is maintained substantially at the desired temperature until pyrolysis declines such that production of desired formation fluids from the formation becomes uneconomical. Parts of the formation that are subjected to pyrolysis may include regions brought into a pyrolysis temperature range by heat transfer from only one heat source.

In certain embodiments, formation fluids including pyrolyzation fluids are produced from the formation. As the temperature of the formation increases, the amount of condensable hydrocarbons in the produced formation fluid may decrease. At high temperatures, the formation may produce mostly methane and/or hydrogen. If the hydrocarbon containing formation is heated throughout an entire pyrolysis range, the formation may produce only small amounts of hydrogen

towards an upper limit of the pyrolysis range. After all of the available hydrogen is depleted, a minimal amount of fluid production from the formation will typically occur.

After pyrolysis of hydrocarbons, a large amount of carbon and some hydrogen may still be present in the formation. A significant portion of carbon remaining in the formation can be produced from the formation in the form of synthesis gas. Synthesis gas generation may take place during stage 3 heating depicted in FIG. 1. Stage 3 may include heating a hydrocarbon containing formation to a temperature sufficient to allow synthesis gas generation. For example, synthesis gas may be produced in a temperature range from about 400 °C to about 1200 °C, about 500 °C to about 1100 °C, or about 550 °C to about 1000 °C. The temperature of the heated portion of the formation when the synthesis gas generating fluid is introduced to the formation determines the composition of synthesis gas produced in the formation. The generated synthesis gas may be removed from the formation through a production well or production wells.

Total energy content of fluids produced from the hydrocarbon containing formation may stay relatively constant throughout pyrolysis and synthesis gas generation. During pyrolysis at relatively low formation temperatures, a significant portion of the produced fluid may be condensable hydrocarbons that have a high energy content. At higher pyrolysis temperatures, however, less of the formation fluid may include condensable hydrocarbons. More non-condensable formation fluids may be produced from the formation. Energy content per unit volume of the produced fluid may decline slightly during generation of predominantly non-condensable formation fluids. During synthesis gas generation, energy content per unit volume of produced synthesis gas declines significantly compared to energy content of pyrolyzation fluid. The volume of the produced synthesis gas, however, will in many instances increase substantially, thereby compensating for the decreased energy content.

FIG. 2 depicts a schematic view of an embodiment of a portion of the in situ heat treatment system for treating the hydrocarbon containing formation. The in situ heat treatment system may include barrier wells 200. Barrier wells are used to form a barrier around a treatment area. The barrier inhibits fluid flow into and/or out of the treatment area. Barrier wells include, but are not limited to, dewatering wells, vacuum wells, capture wells, injection wells, grout wells, freeze wells, or combinations thereof. In some embodiments, barrier wells 200 are dewatering wells. Dewatering wells may remove liquid water and/or inhibit liquid water from entering a portion of the formation to be heated, or to the formation being heated. In the embodiment depicted in FIG. 2, the barrier wells 200 are shown extending only along one side of heat sources 202, but the barrier wells typically encircle all heat sources 202 used, or to be used, to heat a treatment area of the formation.

Heat sources 202 are placed in at least a portion of the formation. Heat sources 202 may include heaters such as insulated conductors, conductor-in-conduit heaters, surface burners,

flameless distributed combustors, and/or natural distributed combustors. Heat sources 202 may also include other types of heaters. Heat sources 202 provide heat to at least a portion of the formation to heat hydrocarbons in the formation. Energy may be supplied to heat sources 202 through supply lines 204. Supply lines 204 may be structurally different depending on the type of heat source or heat sources used to heat the formation. Supply lines 204 for heat sources may transmit electricity for electric heaters, may transport fuel for combustors, or may transport heat exchange fluid that is circulated in the formation. In some embodiments, electricity for an in situ heat treatment process may be provided by a nuclear power plant or nuclear power plants. The use of nuclear power may allow for reduction or elimination of carbon dioxide emissions from the in situ heat treatment process.

Production wells 206 are used to remove formation fluid from the formation. In some embodiments, production well 206 includes a heat source. The heat source in the production well may heat one or more portions of the formation at or near the production well. In some in situ heat treatment process embodiments, the amount of heat supplied to the formation from the production well per meter of the production well is less than the amount of heat applied to the formation from a heat source that heats the formation per meter of the heat source. Heat applied to the formation from the production well may increase formation permeability adjacent to the production well by vaporizing and removing liquid phase fluid adjacent to the production well and/or by increasing the permeability of the formation adjacent to the production well by formation of macro and/or micro fractures.

In some embodiments, the heat source in production well 206 allows for vapor phase removal of formation fluids from the formation. Providing heating at or through the production well may: (1) inhibit condensation and/or refluxing of production fluid when such production fluid is moving in the production well proximate the overburden, (2) increase heat input into the formation, (3) increase production rate from the production well as compared to a production well without a heat source, (4) inhibit condensation of high carbon number compounds (C<sub>6</sub> and above) in the production well, and/or (5) increase formation permeability at or proximate the production well.

Subsurface pressure in the formation may correspond to the fluid pressure generated in the formation. As temperatures in the heated portion of the formation increase, the pressure in the heated portion may increase as a result of increased fluid generation and vaporization of water. Controlling rate of fluid removal from the formation may allow for control of pressure in the formation. Pressure in the formation may be determined at a number of different locations, such as near or at production wells, near or at heat sources, or at monitor wells.

In some hydrocarbon containing formations, production of hydrocarbons from the formation is inhibited until at least some hydrocarbons in the formation have been pyrolyzed.

Formation fluid may be produced from the formation when the formation fluid is of a selected quality. In some embodiments, the selected quality includes an API gravity of at least about 20°, 30°, or 40°. Inhibiting production until at least some hydrocarbons are pyrolyzed may increase conversion of heavy hydrocarbons to light hydrocarbons. Inhibiting initial production may minimize the production of heavy hydrocarbons from the formation. Production of substantial amounts of heavy hydrocarbons may require expensive equipment and/or reduce the life of production equipment.

After pyrolysis temperatures are reached and production from the formation is allowed, pressure in the formation may be varied to alter and/or control a composition of formation fluid produced, to control a percentage of condensable fluid as compared to non-condensable fluid in the formation fluid, and/or to control an API gravity of formation fluid being produced. For example, decreasing pressure may result in production of a larger condensable fluid component. The condensable fluid component may contain a larger percentage of olefins.

In some in situ heat treatment process embodiments, pressure in the formation may be maintained high enough to promote production of formation fluid with an API gravity of greater than 20°. Maintaining increased pressure in the formation may inhibit formation subsidence during in situ heat treatment. Maintaining increased pressure may facilitate vapor phase production of fluids from the formation. Vapor phase production may allow for a reduction in size of collection conduits used to transport fluids produced from the formation. Maintaining increased pressure may reduce or eliminate the need to compress formation fluids at the surface to transport the fluids in collection conduits to treatment facilities.

Maintaining increased pressure in a heated portion of the formation may surprisingly allow for production of large quantities of hydrocarbons of increased quality and of relatively low molecular weight. Pressure may be maintained so that formation fluid produced has a minimal amount of compounds above a selected carbon number. The selected carbon number may be at most 25, at most 20, at most 12, or at most 8. Some high carbon number compounds may be entrained in vapor in the formation and may be removed from the formation with the vapor. Maintaining increased pressure in the formation may inhibit entrainment of high carbon number compounds and/or multi-ring hydrocarbon compounds in the vapor. High carbon number compounds and/or multi-ring hydrocarbon compounds may remain in a liquid phase in the formation for significant time periods. The significant time periods may provide sufficient time for the compounds to pyrolyze to form lower carbon number compounds.

Formation fluid produced from production wells 206 may be transported through collection piping 208 to treatment facilities 210. Formation fluids may also be produced from heat sources 202. For example, fluid may be produced from heat sources 202 to control pressure in the formation adjacent to the heat sources. Fluid produced from heat sources 202 may be transported

through tubing or piping to collection piping 208 or the produced fluid may be transported through tubing or piping directly to treatment facilities 210. Treatment facilities 210 may include separation units, reaction units, upgrading units, fuel cells, turbines, storage vessels, and/or other systems and units for processing produced formation fluids. The treatment facilities may form transportation fuel from at least a portion of the hydrocarbons produced from the formation. In some embodiments, the transportation fuel may be jet fuel, such as JP-8.

Temperature limited heaters may be in configurations and/or may include materials that provide automatic temperature limiting properties for the heater at certain temperatures. In certain embodiments, ferromagnetic materials are used in temperature limited heaters. Ferromagnetic material may self-limit temperature at or near the Curie temperature of the material and/or the phase transformation temperature range to provide a reduced amount of heat when a time-varying current is applied to the material. In certain embodiments, the ferromagnetic material self-limits temperature of the temperature limited heater at a selected temperature that is approximately the Curie temperature and/or in the phase transformation temperature range. In certain embodiments, the selected temperature is within about 35 °C, within about 25 °C, within about 20 °C, or within about 10 °C of the Curie temperature and/or the phase transformation temperature range. In certain embodiments, ferromagnetic materials are coupled with other materials (for example, highly conductive materials, high strength materials, corrosion resistant materials, or combinations thereof) to provide various electrical and/or mechanical properties. Some parts of the temperature limited heater may have a lower resistance (caused by different geometries and/or by using different ferromagnetic and/or non-ferromagnetic materials) than other parts of the temperature limited heater. Having parts of the temperature limited heater with various materials and/or dimensions allows for tailoring the desired heat output from each part of the heater.

Temperature limited heaters may be more reliable than other heaters. Temperature limited heaters may be less apt to break down or fail due to hot spots in the formation. In some embodiments, temperature limited heaters allow for substantially uniform heating of the formation. In some embodiments, temperature limited heaters are able to heat the formation more efficiently by operating at a higher average heat output along the entire length of the heater. The temperature limited heater operates at the higher average heat output along the entire length of the heater because power to the heater does not have to be reduced to the entire heater, as is the case with typical constant wattage heaters, if a temperature along any point of the heater exceeds, or is about to exceed, a maximum operating temperature of the heater. Heat output from portions of a temperature limited heater approaching a Curie temperature and/or the phase transformation temperature range of the heater automatically reduces without controlled adjustment of the time-varying current applied to the heater. The heat output automatically reduces due to changes in electrical properties (for example, electrical resistance) of portions of the temperature limited

heater. Thus, more power is supplied by the temperature limited heater during a greater portion of a heating process.

In certain embodiments, the system including temperature limited heaters initially provides a first heat output and then provides a reduced (second heat output) heat output, near, at, or above the Curie temperature and/or the phase transformation temperature range of an electrically resistive portion of the heater when the temperature limited heater is energized by a time-varying current. The first heat output is the heat output at temperatures below which the temperature limited heater begins to self-limit. In some embodiments, the first heat output is the heat output at a temperature about 50 °C, about 75 °C, about 100 °C, or about 125 °C below the Curie temperature and/or the phase transformation temperature range of the ferromagnetic material in the temperature limited heater.

The temperature limited heater may be energized by time-varying current (alternating current or modulated direct current) supplied at the wellhead. The wellhead may include a power source and other components (for example, modulation components, transformers, and/or capacitors) used in supplying power to the temperature limited heater. The temperature limited heater may be one of many heaters used to heat a portion of the formation.

In certain embodiments, the temperature limited heater includes a conductor that operates as a skin effect or proximity effect heater when time-varying current is applied to the conductor. The skin effect limits the depth of current penetration into the interior of the conductor. For ferromagnetic materials, the skin effect is dominated by the magnetic permeability of the conductor. The relative magnetic permeability of ferromagnetic materials is typically between 10 and 1000 (for example, the relative magnetic permeability of ferromagnetic materials is typically at least 10 and may be at least 50, 100, 500, 1000 or greater). As the temperature of the ferromagnetic material is raised above the Curie temperature, or the phase transformation temperature range, and/or as the applied electrical current is increased, the magnetic permeability of the ferromagnetic material decreases substantially and the skin depth expands rapidly (for example, the skin depth expands as the inverse square root of the magnetic permeability). The reduction in magnetic permeability results in a decrease in the AC or modulated DC resistance of the conductor near, at, or above the Curie temperature, the phase transformation temperature range, and/or as the applied electrical current is increased. When the temperature limited heater is powered by a substantially constant current source, portions of the heater that approach, reach, or are above the Curie temperature and/or the phase transformation temperature range may have reduced heat dissipation. Sections of the temperature limited heater that are not at or near the Curie temperature and/or the phase transformation temperature range may be dominated by skin effect heating that allows the heater to have high heat dissipation due to a higher resistive load.

Curie temperature heaters have been used in soldering equipment, heaters for medical applications, and heating elements for ovens (for example, pizza ovens). Some of these uses are disclosed in U.S. Patent Nos. 5,579,575 to Lamome et al.; 5,065,501 to Henschen et al.; and 5,512,732 to Yagnik et al. U.S. Patent No. 4,849,611 to Whitney et al. describes a plurality of  
5 discrete, spaced-apart heating units including a reactive component, a resistive heating component, and a temperature responsive component.

An advantage of using the temperature limited heater to heat hydrocarbons in the formation is that the conductor is chosen to have a Curie temperature and/or a phase transformation temperature range in a desired range of temperature operation. Operation within the desired  
10 operating temperature range allows substantial heat injection into the formation while maintaining the temperature of the temperature limited heater, and other equipment, below design limit temperatures. Design limit temperatures are temperatures at which properties such as corrosion, creep, and/or deformation are adversely affected. The temperature limiting properties of the temperature limited heater inhibit overheating or burnout of the heater adjacent to low thermal  
15 conductivity "hot spots" in the formation. In some embodiments, the temperature limited heater is able to lower or control heat output and/or withstand heat at temperatures above 25 °C, 37 °C, 100 °C, 250 °C, 500 °C, 700 °C, 800 °C, 900 °C, or higher up to 1131 °C, depending on the materials used in the heater.

The temperature limited heater allows for more heat injection into the formation than  
20 constant wattage heaters because the energy input into the temperature limited heater does not have to be limited to accommodate low thermal conductivity regions adjacent to the heater. For example, in Green River oil shale there is a difference of at least a factor of 3 in the thermal conductivity of the lowest richness oil shale layers and the highest richness oil shale layers. When heating such a formation, substantially more heat is transferred to the formation with the  
25 temperature limited heater than with the conventional heater that is limited by the temperature at low thermal conductivity layers. The heat output along the entire length of the conventional heater needs to accommodate the low thermal conductivity layers so that the heater does not overheat at the low thermal conductivity layers and burn out. The heat output adjacent to the low thermal conductivity layers that are at high temperature will reduce for the temperature limited heater, but  
30 the remaining portions of the temperature limited heater that are not at high temperature will still provide high heat output. Because heaters for heating hydrocarbon formations typically have long lengths (for example, at least 10 m, 100 m, 300 m, 500 m, 1 km or more up to about 10 km), the majority of the length of the temperature limited heater may be operating below the Curie temperature while only a few portions are at or near the Curie temperature and/or the phase  
35 transformation temperature range of the temperature limited heater.

The use of temperature limited heaters allows for efficient transfer of heat to the formation. Efficient transfer of heat allows for reduction in time needed to heat the formation to a desired temperature. For example, in Green River oil shale, pyrolysis typically requires 9.5 years to 10 years of heating when using a 12 m heater well spacing with conventional constant wattage heaters.

5 For the same heater spacing, temperature limited heaters may allow a larger average heat output while maintaining heater equipment temperatures below equipment design limit temperatures. Pyrolysis in the formation may occur at an earlier time with the larger average heat output provided by temperature limited heaters than the lower average heat output provided by constant wattage heaters. For example, in Green River oil shale, pyrolysis may occur in 5 years using temperature

10 limited heaters with a 12 m heater well spacing. Temperature limited heaters counteract hot spots due to inaccurate well spacing or drilling where heater wells come too close together. In certain embodiments, temperature limited heaters allow for increased power output over time for heater wells that have been spaced too far apart, or limit power output for heater wells that are spaced too close together. Temperature limited heaters also supply more power in regions adjacent the

15 overburden and underburden to compensate for temperature losses in these regions.

Temperature limited heaters may be advantageously used in many types of formations. For example, in tar sands formations or relatively permeable formations containing heavy hydrocarbons, temperature limited heaters may be used to provide a controllable low temperature output for reducing the viscosity of fluids, mobilizing fluids, and/or enhancing the radial flow of

20 fluids at or near the wellbore or in the formation. Temperature limited heaters may be used to inhibit excess coke formation due to overheating of the near wellbore region of the formation.

The use of temperature limited heaters, in some embodiments, eliminates or reduces the need for expensive temperature control circuitry. For example, the use of temperature limited heaters eliminates or reduces the need to perform temperature logging and/or the need to use fixed

25 thermocouples on the heaters to monitor potential overheating at hot spots.

In certain embodiments, phase transformation (for example, crystalline phase transformation or a change in the crystal structure) of materials used in a temperature limited heater change the selected temperature at which the heater self-limits. Ferromagnetic material used in the temperature limited heater may have a phase transformation (for example, a transformation from ferrite to austenite)

30 that decreases the magnetic permeability of the ferromagnetic material. This reduction in magnetic permeability is similar to reduction in magnetic permeability due to the magnetic transition of the ferromagnetic material at the Curie temperature. The Curie temperature is the magnetic transition temperature of the ferrite phase of the ferromagnetic material. The reduction in magnetic permeability results in a decrease in the AC or modulated DC resistance of the temperature limited

35 heater near, at, or above the temperature of the phase transformation and/or the Curie temperature of the ferromagnetic material.



The phase transformation of the ferromagnetic material may occur over a temperature range. The temperature range of the phase transformation depends on the ferromagnetic material and may vary, for example, over a range of about 5 °C to a range of about 200 °C. Because the phase transformation takes place over a temperature range, the reduction in the magnetic permeability due to the phase transformation takes place over the temperature range. The reduction in magnetic permeability may also occur hysteretically over the temperature range of the phase transformation. In some embodiments, the phase transformation back to the lower temperature phase of the ferromagnetic material is slower than the phase transformation to the higher temperature phase (for example, the transition from austenite back to ferrite is slower than the transition from ferrite to austenite). The slower phase transformation back to the lower temperature phase may cause hysteretic operation of the heater at or near the phase transformation temperature range that allows the heater to slowly increase to higher resistance after the resistance of the heater reduces due to high temperature.

In some embodiments, the phase transformation temperature range overlaps with the reduction in the magnetic permeability when the temperature approaches the Curie temperature of the ferromagnetic material. The overlap may produce a faster drop in electrical resistance versus temperature than if the reduction in magnetic permeability is solely due to the temperature approaching the Curie temperature. The overlap may also produce hysteretic behavior of the temperature limited heater near the Curie temperature and/or in the phase transformation temperature range.

In certain embodiments, the hysteretic operation due to the phase transformation is a smoother transition than the reduction in magnetic permeability due to magnetic transition at the Curie temperature. The smoother transition may be easier to control (for example, electrical control using a process control device that interacts with the power supply) than the sharper transition at the Curie temperature. In some embodiments, the Curie temperature is located inside the phase transformation range for selected metallurgies used in temperature limited heaters. This phenomenon provides temperature limited heaters with the smooth transition properties of the phase transformation in addition to a sharp and definite transition due to the reduction in magnetic properties at the Curie temperature. Such temperature limited heaters may be easy to control (due to the phase transformation) while providing finite temperature limits (due to the sharp Curie temperature transition). Using the phase transformation temperature range instead of and/or in addition to the Curie temperature in temperature limited heaters increases the number and range of metallurgies that may be used for temperature limited heaters.

In certain embodiments, alloy additions are made to the ferromagnetic material to adjust the temperature range of the phase transformation. For example, adding carbon to the ferromagnetic material may increase the phase transformation temperature range and lower the

onset temperature of the phase transformation. Adding titanium to the ferromagnetic material may increase the onset temperature of the phase transformation and decrease the phase transformation temperature range. Alloy compositions may be adjusted to provide desired Curie temperature and phase transformation properties for the ferromagnetic material. The alloy composition of the ferromagnetic material may be chosen based on desired properties for the ferromagnetic material (such as, but not limited to, magnetic permeability transition temperature or temperature range, resistance versus temperature profile, or power output). Addition of titanium may allow higher Curie temperatures to be obtained when adding cobalt to 410 stainless steel by raising the ferrite to austenite phase transformation temperature range to a temperature range that is above, or well above, the Curie temperature of the ferromagnetic material.

In some embodiments, temperature limited heaters are more economical to manufacture or make than standard heaters. Typical ferromagnetic materials include iron, carbon steel, or ferritic stainless steel. Such materials are inexpensive as compared to nickel-based heating alloys (such as nichrome, Kanthal™ (Bulten-Kanthal AB, Sweden), and/or LOHM™ (Driver-Harris Company, Harrison, New Jersey, U.S.A.)) typically used in insulated conductor (mineral insulated cable) heaters. In one embodiment of the temperature limited heater, the temperature limited heater is manufactured in continuous lengths as an insulated conductor heater to lower costs and improve reliability.

FIGS. 3-12 depict various embodiments of temperature limited heaters. One or more features of an embodiment of the temperature limited heater depicted in any of these figures may be combined with one or more features of other embodiments of temperature limited heaters depicted in these figures. In certain embodiments described herein, temperature limited heaters are dimensioned to operate at a frequency of 60 Hz AC. It is to be understood that dimensions of the temperature limited heater may be adjusted from those described herein to operate in a similar manner at other AC frequencies or with modulated DC current.

FIG. 3 depicts a cross-sectional representation of an embodiment of the temperature limited heater with an outer conductor having a ferromagnetic section and a non-ferromagnetic section. FIGS. 4 and 5 depict transverse cross-sectional views of the embodiment shown in FIG. 3. In one embodiment, ferromagnetic section 212 is used to provide heat to hydrocarbon layers in the formation. Non-ferromagnetic section 214 is used in the overburden of the formation. Non-ferromagnetic section 214 provides little or no heat to the overburden, thus inhibiting heat losses in the overburden and improving heater efficiency. Ferromagnetic section 212 includes a ferromagnetic material such as 409 stainless steel or 410 stainless steel. Ferromagnetic section 212 has a thickness of 0.3 cm. Non-ferromagnetic section 214 is copper with a thickness of 0.3 cm. Inner conductor 216 is copper. Inner conductor 216 has a diameter of 0.9 cm. Electrical insulator

218 is silicon nitride, boron nitride, magnesium oxide powder, or another suitable insulator material. Electrical insulator 218 has a thickness of 0.1 cm to 0.3 cm.

FIG. 6 depicts a cross-sectional representation of an embodiment of a temperature limited heater with an outer conductor having a ferromagnetic section and a non-ferromagnetic section placed inside a sheath. FIGS. 7, 8, and 9 depict transverse cross-sectional views of the embodiment shown in FIG. 6. Ferromagnetic section 212 is 410 stainless steel with a thickness of 0.6 cm. Non-ferromagnetic section 214 is copper with a thickness of 0.6 cm. Inner conductor 216 is copper with a diameter of 0.9 cm. Outer conductor 220 includes ferromagnetic material. Outer conductor 220 provides some heat in the overburden section of the heater. Providing some heat in the overburden inhibits condensation or refluxing of fluids in the overburden. Outer conductor 220 is 409, 410, or 446 stainless steel with an outer diameter of 3.0 cm and a thickness of 0.6 cm. Electrical insulator 218 includes compacted magnesium oxide powder with a thickness of 0.3 cm. In some embodiments, electrical insulator 218 includes silicon nitride, boron nitride, or hexagonal type boron nitride. Conductive section 222 may couple inner conductor 216 with ferromagnetic section 212 and/or outer conductor 220.

For a temperature limited heater in which the ferromagnetic conductor provides a majority of the resistive heat output below the Curie temperature and/or the phase transformation temperature range, a majority of the current flows through material with highly non-linear functions of magnetic field (H) versus magnetic induction (B). These non-linear functions may cause strong inductive effects and distortion that lead to decreased power factor in the temperature limited heater at temperatures below the Curie temperature and/or the phase transformation temperature range. These effects may render the electrical power supply to the temperature limited heater difficult to control and may result in additional current flow through surface and/or overburden power supply conductors. Expensive and/or difficult to implement control systems such as variable capacitors or modulated power supplies may be used to compensate for these effects and to control temperature limited heaters where the majority of the resistive heat output is provided by current flow through the ferromagnetic material.

In certain temperature limited heater embodiments, the ferromagnetic conductor confines a majority of the flow of electrical current to an electrical conductor coupled to the ferromagnetic conductor when the temperature limited heater is below or near the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor. The electrical conductor may be a sheath, jacket, support member, corrosion resistant member, or other electrically resistive member. In some embodiments, the ferromagnetic conductor confines a majority of the flow of electrical current to the electrical conductor positioned between an outermost layer and the ferromagnetic conductor. The ferromagnetic conductor is located in the cross section of the temperature limited heater such that the magnetic properties of the ferromagnetic conductor at or

below the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor confine the majority of the flow of electrical current to the electrical conductor. The majority of the flow of electrical current is confined to the electrical conductor due to the skin effect of the ferromagnetic conductor. Thus, the majority of the current is flowing  
5 through material with substantially linear resistive properties throughout most of the operating range of the heater.

In certain embodiments, the ferromagnetic conductor and the electrical conductor are located in the cross section of the temperature limited heater so that the skin effect of the ferromagnetic material limits the penetration depth of electrical current in the electrical conductor  
10 and the ferromagnetic conductor at temperatures below the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor. Thus, the electrical conductor provides a majority of the electrically resistive heat output of the temperature limited heater at temperatures up to a temperature at or near the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor. In certain embodiments, the dimensions of the  
15 electrical conductor may be chosen to provide desired heat output characteristics.

Because the majority of the current flows through the electrical conductor below the Curie temperature and/or the phase transformation temperature range, the temperature limited heater has a resistance versus temperature profile that at least partially reflects the resistance versus temperature profile of the material in the electrical conductor. Thus, the resistance versus  
20 temperature profile of the temperature limited heater is substantially linear below the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor if the material in the electrical conductor has a substantially linear resistance versus temperature profile. The resistance of the temperature limited heater has little or no dependence on the current flowing through the heater until the temperature nears the Curie temperature and/or the phase  
25 transformation temperature range. The majority of the current flows in the electrical conductor rather than the ferromagnetic conductor below the Curie temperature and/or the phase transformation temperature range.

Resistance versus temperature profiles for temperature limited heaters in which the majority of the current flows in the electrical conductor also tend to exhibit sharper reductions in  
30 resistance near or at the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor. The sharper reductions in resistance near or at the Curie temperature and/or the phase transformation temperature range may be easier to control than more gradual resistance reductions near the Curie temperature and/or the phase transformation temperature range because little current is flowing through the ferromagnetic material.

In certain embodiments, the material and/or the dimensions of the material in the electrical conductor are selected so that the temperature limited heater has a desired resistance versus  
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temperature profile below the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor.

Temperature limited heaters in which the majority of the current flows in the electrical conductor rather than the ferromagnetic conductor below the Curie temperature and/or the phase transformation temperature range are easier to predict and/or control. Behavior of temperature limited heaters in which the majority of the current flows in the electrical conductor rather than the ferromagnetic conductor below the Curie temperature and/or the phase transformation temperature range may be predicted by, for example, its resistance versus temperature profile and/or its power factor versus temperature profile. Resistance versus temperature profiles and/or power factor versus temperature profiles may be assessed or predicted by, for example, experimental measurements that assess the behavior of the temperature limited heater, analytical equations that assess or predict the behavior of the temperature limited heater, and/or simulations that assess or predict the behavior of the temperature limited heater.

In certain embodiments, assessed or predicted behavior of the temperature limited heater is used to control the temperature limited heater. The temperature limited heater may be controlled based on measurements (assessments) of the resistance and/or the power factor during operation of the heater. In some embodiments, the power, or current, supplied to the temperature limited heater is controlled based on assessment of the resistance and/or the power factor of the heater during operation of the heater and the comparison of this assessment versus the predicted behavior of the heater. In certain embodiments, the temperature limited heater is controlled without measurement of the temperature of the heater or a temperature near the heater. Controlling the temperature limited heater without temperature measurement eliminates operating costs associated with downhole temperature measurement. Controlling the temperature limited heater based on assessment of the resistance and/or the power factor of the heater also reduces the time for making adjustments in the power or current supplied to the heater compared to controlling the heater based on measured temperature.

As the temperature of the temperature limited heater approaches or exceeds the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor, reduction in the ferromagnetic properties of the ferromagnetic conductor allows electrical current to flow through a greater portion of the electrically conducting cross section of the temperature limited heater. Thus, the electrical resistance of the temperature limited heater is reduced and the temperature limited heater automatically provides reduced heat output at or near the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor. In certain embodiments, a highly electrically conductive member is coupled to the ferromagnetic conductor and the electrical conductor to reduce the electrical resistance of the temperature limited heater at or above the Curie temperature and/or the phase transformation temperature range of the

ferromagnetic conductor. The highly electrically conductive member may be an inner conductor, a core, or another conductive member of copper, aluminum, nickel, or alloys thereof.

The ferromagnetic conductor that confines the majority of the flow of electrical current to the electrical conductor at temperatures below the Curie temperature and/or the phase transformation temperature range may have a relatively small cross section compared to the ferromagnetic conductor in temperature limited heaters that use the ferromagnetic conductor to provide the majority of resistive heat output up to or near the Curie temperature and/or the phase transformation temperature range. A temperature limited heater that uses the electrical conductor to provide a majority of the resistive heat output below the Curie temperature and/or the phase transformation temperature range has low magnetic inductance at temperatures below the Curie temperature and/or the phase transformation temperature range because less current is flowing through the ferromagnetic conductor as compared to the temperature limited heater where the majority of the resistive heat output below the Curie temperature and/or the phase transformation temperature range is provided by the ferromagnetic material. Magnetic field (H) at radius (r) of the ferromagnetic conductor is proportional to the current (I) flowing through the ferromagnetic conductor and the core divided by the radius, or:

$$(1) \quad H \propto I/r.$$

Since only a portion of the current flows through the ferromagnetic conductor for a temperature limited heater that uses the outer conductor to provide a majority of the resistive heat output below the Curie temperature and/or the phase transformation temperature range, the magnetic field of the temperature limited heater may be significantly smaller than the magnetic field of the temperature limited heater where the majority of the current flows through the ferromagnetic material. The relative magnetic permeability ( $\mu$ ) may be large for small magnetic fields.

The skin depth ( $\delta$ ) of the ferromagnetic conductor is inversely proportional to the square root of the relative magnetic permeability ( $\mu$ ):

$$(2) \quad \delta \propto (1/\mu)^{1/2}.$$

Increasing the relative magnetic permeability decreases the skin depth of the ferromagnetic conductor. However, because only a portion of the current flows through the ferromagnetic conductor for temperatures below the Curie temperature and/or the phase transformation temperature range, the radius (or thickness) of the ferromagnetic conductor may be decreased for ferromagnetic materials with large relative magnetic permeabilities to compensate for the decreased skin depth while still allowing the skin effect to limit the penetration depth of the electrical current to the electrical conductor at temperatures below the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor. The radius (thickness) of the ferromagnetic conductor may be between 0.3 mm and 8 mm, between 0.3 mm and 2 mm, or between 2 mm and 4 mm depending on the relative magnetic permeability of the ferromagnetic

conductor. Decreasing the thickness of the ferromagnetic conductor decreases costs of manufacturing the temperature limited heater, as the cost of ferromagnetic material tends to be a significant portion of the cost of the temperature limited heater. Increasing the relative magnetic permeability of the ferromagnetic conductor provides a higher turndown ratio and a sharper  
5 decrease in electrical resistance for the temperature limited heater at or near the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor.

Ferromagnetic materials (such as purified iron or iron-cobalt alloys) with high relative magnetic permeabilities (for example, at least 200, at least 1000, at least  $1 \times 10^4$ , or at least  $1 \times 10^5$ ) and/or high Curie temperatures (for example, at least 600 °C, at least 700 °C, or at least 800 °C)  
10 tend to have less corrosion resistance and/or less mechanical strength at high temperatures. The electrical conductor may provide corrosion resistance and/or high mechanical strength at high temperatures for the temperature limited heater. Thus, the ferromagnetic conductor may be chosen primarily for its ferromagnetic properties.

Confining the majority of the flow of electrical current to the electrical conductor below the  
15 Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor reduces variations in the power factor. Because only a portion of the electrical current flows through the ferromagnetic conductor below the Curie temperature and/or the phase transformation temperature range, the non-linear ferromagnetic properties of the ferromagnetic conductor have little or no effect on the power factor of the temperature limited heater, except at or  
20 near the Curie temperature and/or the phase transformation temperature range. Even at or near the Curie temperature and/or the phase transformation temperature range, the effect on the power factor is reduced compared to temperature limited heaters in which the ferromagnetic conductor provides a majority of the resistive heat output below the Curie temperature and/or the phase transformation temperature range. Thus, there is less or no need for external compensation (for example, variable  
25 capacitors or waveform modification) to adjust for changes in the inductive load of the temperature limited heater to maintain a relatively high power factor.

FIG. 10 depicts an embodiment of a temperature limited heater in which the support member provides a majority of the heat output below the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor. Core 226 is an inner conductor  
30 of the temperature limited heater. In certain embodiments, core 226 is a highly electrically conductive material such as copper or aluminum. In some embodiments, core 226 is a copper alloy that provides mechanical strength and good electrical conductivity such as a dispersion strengthened copper. In one embodiment, core 226 is Glidcop® (SCM Metal Products, Inc., Research Triangle Park, North Carolina, U.S.A.). Ferromagnetic conductor 228 is a thin layer of  
35 ferromagnetic material between electrical conductor 232 and core 226. In certain embodiments, electrical conductor 232 is also support member 230. In certain embodiments, ferromagnetic

conductor 228 is iron or an iron alloy. In some embodiments, ferromagnetic conductor 228 includes ferromagnetic material with a high relative magnetic permeability. For example, ferromagnetic conductor 228 may be purified iron such as Armco ingot iron (AK Steel Ltd., United Kingdom). Iron with some impurities typically has a relative magnetic permeability on the order of 400. Purifying the iron by annealing the iron in hydrogen gas (H<sub>2</sub>) at 1450 °C increases the relative magnetic permeability of the iron. Increasing the relative magnetic permeability of ferromagnetic conductor 228 allows the thickness of the ferromagnetic conductor to be reduced. For example, the thickness of unpurified iron may be approximately 4.5 mm while the thickness of the purified iron is approximately 0.76 mm.

In certain embodiments, electrical conductor 232 provides support for ferromagnetic conductor 228 and the temperature limited heater. Electrical conductor 232 may be made of a material that provides good mechanical strength at temperatures near or above the Curie temperature and/or the phase transformation temperature range of ferromagnetic conductor 228. In certain embodiments, electrical conductor 232 is a corrosion resistant member. Electrical conductor 232 (support member 230) may provide support for ferromagnetic conductor 228 and corrosion resistance. Electrical conductor 232 is made from a material that provides desired electrically resistive heat output at temperatures up to and/or above the Curie temperature and/or the phase transformation temperature range of ferromagnetic conductor 228.

In an embodiment, electrical conductor 232 is 347H stainless steel. In some embodiments, electrical conductor 232 is another electrically conductive, good mechanical strength, corrosion resistant material. For example, electrical conductor 232 may be 304H, 316H, 347HH, NF709, Incoloy® 800H alloy (Inco Alloys International, Huntington, West Virginia, U.S.A.), Haynes® HR120® alloy, or Inconel® 617 alloy.

In some embodiments, electrical conductor 232 (support member 230) includes different alloys in different portions of the temperature limited heater. For example, a lower portion of electrical conductor 232 (support member 230) is 347H stainless steel and an upper portion of the electrical conductor (support member) is NF709. In certain embodiments, different alloys are used in different portions of the electrical conductor (support member) to increase the mechanical strength of the electrical conductor (support member) while maintaining desired heating properties for the temperature limited heater.

In some embodiments, ferromagnetic conductor 228 includes different ferromagnetic conductors in different portions of the temperature limited heater. Different ferromagnetic conductors may be used in different portions of the temperature limited heater to vary the Curie temperature and/or the phase transformation temperature range and, thus, the maximum operating temperature in the different portions. In some embodiments, the Curie temperature in an upper portion of the temperature limited heater is lower than the Curie temperature in a lower portion of



the heater. The lower Curie temperature in the upper portion increases the creep-rupture strength lifetime in the upper portion of the heater.

In the embodiment depicted in FIG. 10, ferromagnetic conductor 228, electrical conductor 232, and core 226 are dimensioned so that the skin depth of the ferromagnetic conductor limits the penetration depth of the majority of the flow of electrical current to the support member when the temperature is below the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor. Thus, electrical conductor 232 provides a majority of the electrically resistive heat output of the temperature limited heater at temperatures up to a temperature at or near the Curie temperature and/or the phase transformation temperature range of ferromagnetic conductor 228. In certain embodiments, the temperature limited heater depicted in FIG. 10 is smaller (for example, an outside diameter of 3 cm, 2.9 cm, 2.5 cm, or less) than other temperature limited heaters that do not use electrical conductor 232 to provide the majority of electrically resistive heat output. The temperature limited heater depicted in FIG. 10 may be smaller because ferromagnetic conductor 228 is thin as compared to the size of the ferromagnetic conductor needed for a temperature limited heater in which the majority of the resistive heat output is provided by the ferromagnetic conductor.

In some embodiments, the support member and the corrosion resistant member are different members in the temperature limited heater. FIGS. 11 and 12 depict embodiments of temperature limited heaters in which the jacket provides a majority of the heat output below the Curie temperature and/or the phase transformation temperature range of the ferromagnetic conductor. In these embodiments, electrical conductor 232 is jacket 224. Electrical conductor 232, ferromagnetic conductor 228, support member 230, and core 226 (in FIG. 11) or inner conductor 216 (in FIG. 12) are dimensioned so that the skin depth of the ferromagnetic conductor limits the penetration depth of the majority of the flow of electrical current to the thickness of the jacket. In certain embodiments, electrical conductor 232 is a material that is corrosion resistant and provides electrically resistive heat output below the Curie temperature and/or the phase transformation temperature range of ferromagnetic conductor 228. For example, electrical conductor 232 is 825 stainless steel or 347H stainless steel. In some embodiments, electrical conductor 232 has a small thickness (for example, on the order of 0.5 mm).

In FIG. 11, core 226 is highly electrically conductive material such as copper or aluminum. Support member 230 is 347H stainless steel or another material with good mechanical strength at or near the Curie temperature and/or the phase transformation temperature range of ferromagnetic conductor 228.

In FIG. 12, support member 230 is the core of the temperature limited heater and is 347H stainless steel or another material with good mechanical strength at or near the Curie temperature

and/or the phase transformation temperature range of ferromagnetic conductor 228. Inner conductor 216 is highly electrically conductive material such as copper or aluminum.

### Examples

Non-restrictive examples are set forth below.

5 FIG. 13 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for iron alloy TC3 (0.1% by weight carbon, 5% by weight cobalt, 12% by weight chromium, 0.5% by weight manganese, 0.5% by weight silicon). Curve 234 depicts weight percentage of the ferrite phase. Curve 236 depicts weight percentage of the austenite phase. The arrow points to the Curie temperature of the alloy. As shown in FIG. 13, the phase transformation  
10 was close to the Curie temperature but did not overlap with the Curie temperature for this alloy.

FIG. 14 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for iron alloy FM-4 (0.1% by weight carbon, 5% by weight cobalt, 0.5% by weight manganese, 0.5% by weight silicon). Curve 238 depicts weight percentage of the ferrite phase. Curve 240 depicts weight percentage of the austenite phase. The arrow points to the Curie  
15 temperature of the alloy. As shown in FIG. 14, the phase transformation broadened without chromium in the alloy and the phase transformation overlapped with the Curie temperature for this alloy.

Calculations for the Curie temperature ( $T_c$ ) and the phase transformation behavior were done for various mixtures of cobalt, carbon, manganese, silicon, vanadium, and titanium using  
20 computational thermodynamic software (ThermoCalc is obtained from Thermo-Calc Software, Inc., (McMurray, PA, U.S.A) and JMatPro is obtained from Sente Software, Ltd., (Guildford, United Kingdom)) to predict the effect of additional elements on Curie Temperature for selected compositions, the temperature ( $A_1$ ) at which ferrite transforms to paramagnetic austenite, and the phases present at those temperatures. An equilibrium calculation temperature of 700 °C was used  
25 in all calculations to determine the Curie temperature of ferrite. As shown in TABLE 1, as the weight percentage of cobalt in the composition increased,  $T_c$  increased and  $A_1$  decreased; however,  $T_c$  remained above  $A_1$ . An increase in the  $A_1$  temperature may be predicted upon sufficient addition of carbide formers vanadium, titanium, niobium, tantalum, and tungsten. For example, about 0.5% by weight of carbide formers may be used in an alloy that includes about 0.1% by  
30 weight of carbon. Addition of carbide formers allows replacement of the  $Fe_3C$  carbide phase with a MC carbide phase. From the calculations, excess amounts of vanadium appeared to not have an impact on  $T_c$ , while excess amounts of other carbide formers reduced the  $T_c$ .

TABLE 1

Composition (% by weight, balance being Fe)						Calculation Results		
Co	C	Mn	Si	V	Ti	T <sub>c</sub> (EC)	A <sub>1</sub> (EC)	Phases Present (~700EC)
0	0.1	0.5	0.5	0	0	758	716	ferrite + Fe <sub>3</sub> C (FM2)
2	0.1	0.5	0.5	0	0	776	726	ferrite + Fe <sub>3</sub> C (FM4)
5	0.1	0.5	0.5	0	0	803	740	ferrite + Fe <sub>3</sub> C (FM6)
8	0.1	0.5	0.5	0	0	829	752	ferrite + Fe <sub>3</sub> C (FM8)
5	0.1	0.5	0.5	0.2	0	803	740	ferrite + Fe <sub>3</sub> C + VC
5	0.1	0.5	0.5	0.4	0	802	773	ferrite + Fe <sub>3</sub> C + VC
5	0.1	0.5	0.5	0.5	0	802	830	ferrite + VC
5	0.1	0.5	0.5	0.6	0	802	855	ferrite + VC
5	0.1	0.5	0.5	0.8	0	803	880	ferrite + VC
5	0.1	0.5	0.5	1.0	0	805	896	ferrite + VC
5	0.1	0.5	0.5	1.5	0	807	928	ferrite + VC
5	0.1	0.5	0.5	2.0	0	810	959	ferrite + VC
6	0.1	0.5	0.5	0.5	0	811	835	ferrite + VC
7	0.1	0.5	0.5	0.5	0	819	839	ferrite + VC
8	0.1	0.5	0.5	0.5	0	828	843	ferrite + VC
9	0.1	0.5	0.5	0.5	0	836	847	ferrite + VC
10	0.1	0.5	0.5	0.5	0	845	852	ferrite + VC
11	0.1	0.5	0.5	0.5	0	853	856	ferrite + VC
12	0.1	0.5	0.5	0.5	0	861	859	ferrite + VC
10	0.1	0.5	0.5	1.0	0	847	907	ferrite + VC
11	0.1	0.5	0.5	1.0	0	855	909	ferrite + VC
12	0.1	0.5	0.5	1.0	0	863	911	ferrite + VC
13	0.1	0.5	0.5	1.0	0	871	913	ferrite + VC
14	0.1	0.5	0.5	1.0	0	879	915	ferrite + VC
15	0.1	0.5	0.5	1.0	0	886	917	ferrite + VC
17	0.1	0.5	0.5	1.0	0	902	920	ferrite + VC
20	0.1	0.5	0.5	1.0	0	924	926	ferrite + VC

Composition (% by weight, balance being Fe)						Calculation Results		
Co	C	Mn	Si	V	Ti	T <sub>c</sub> (EC)	A <sub>1</sub> (EC)	Phases Present (~700EC)
5	0.1	0.5	0.5	0	0.2	802	738	ferrite + Fe <sub>3</sub> C + TiC
5	0.1	0.5	0.5	0	0.3	802	738	ferrite + Fe <sub>3</sub> C + TiC
5	0.1	0.5	0.5	0	0.4	802	867	ferrite + TiC
5	0.1	0.5	0.5	0	0.45	802	896	ferrite + TiC
5	0.1	0.5	0.5	0	0.5	801	902	ferrite + TiC
5	0.1	0.5	0.5	0	1.0	795	934	ferrite + TiC
8	0.1	0.5	0.5	0	0.5	827	905	ferrite + TiC
10	0.1	0.5	0.5	0	0.5	844	908	ferrite + TiC
11	0.1	0.5	0.5	0	0.5	852	909	ferrite + TiC
12	0.1	0.5	0.5	0	0.5	860	911	ferrite + TiC
13	0.1	0.5	0.5	0	0.5	868	912	ferrite + TiC
14	0.1	0.5	0.5	0	0.5	876	914	ferrite + TiC
15	0.1	0.5	0.5	0	0.5	884	915	ferrite + TiC
17	0.1	0.5	0.5	0	0.5	899	918	ferrite + TiC
18	0.1	0.5	0.5	0	0.5	907	920	ferrite + TiC
19	0.1	0.5	0.5	0	0.5	914	921	ferrite + TiC
20	0.1	0.5	0.5	0	0.5	922	923	ferrite + TiC
21	0.1	0.5	0.5	0	0.5	929	924	ferrite + TiC
21	0.1	0.5	0.5	0	0.6	928	926	ferrite + TiC
21	0.1	0.5	0.5	0	0.7	926	928	ferrite + TiC
21	0.1	0.5	0.5	0	0.8	925	930	ferrite + TiC
21	0.1	0.5	0.5	0	1.0	922	934	ferrite + TiC
22	0.1	0.5	0.5	0	1.0	930	935	ferrite + TiC
23	0.1	0.5	0.5	0	1.0	937	936	ferrite + TiC

Several iron-cobalt alloys were prepared and their compositions are given in TABLE 2. These cast alloys were processed into rod and wire, and the measured and calculated T<sub>c</sub> for the rods are listed.

Averages of cooling and heating T<sub>c</sub> measurements were used since no irreversible hysteresis effect

5 was observed during heating and cooling. As shown in TABLE 2, the agreement between calculated T<sub>c</sub> and the measured T<sub>c</sub> was acceptable.

The measured  $T_c$  were performed by a torus technique in which a torus was wound with the sample material. A thermocouple was attached midway along the length.

TABLE 2.

Alloy Designation	Nominal Composition (% by weight, balance being Fe)				$T_c$ (EC) (torus technique)	$T_c$ (EC) (calculated)
	Co	C	Mn	Si		
FM1	0	0	0	0	768	770
FM2	0	0.1	0.5	0.5	--	758
FM3	5	0	0	0	--	818
FM4	5	0.1	0.5	0.5	--	803
FM5	8	0	0	0	--	842
FM6	8	0.1	0.5	0.5	--	826
FM7	10	0	0	0	863	859
FM8	10	0.1	0.5	0.5	--	846

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FIG. 15 depicts the Curie temperature (horizontal bars) and phase transformation temperature range (slashed vertical bars) for several iron alloys. Column 242 is for FM-2 iron-cobalt alloy. Column 244 is for FM-4 iron-cobalt alloy. Column 246 is for FM-6 iron-cobalt alloy. Column 248 is for FM-8 iron-cobalt alloy. Column 250 is for TC1 410 stainless steel alloy with cobalt. Column 252 is for TC2 410 stainless steel alloy with cobalt. Column 254 is for TC3 410 stainless steel alloy with cobalt. Column 256 is for TC4 410 stainless steel alloy with cobalt. Column 258 is for TC5 410 stainless steel alloy with cobalt. As shown in FIG. 15, the iron-cobalt alloys (FM-2, FM-4, FM-6, FM-8) had large phase transformation temperature ranges that overlap with the Curie temperature. The 410 stainless steel alloys with cobalt (TC1, TC2, TC3, TC4, TC5) had small phase transformation temperature ranges. The phase transformation temperature ranges for TC1, TC2, and TC3 were above the Curie temperature. The phase transformation temperature range for TC4 was below the Curie temperature. Thus, a temperature limited heater using TC4 may self-limit at a temperature below the Curie temperature of the TC4.

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FIGS. 16-19 depict the effects of alloy addition to iron-cobalt alloys. FIGS. 16 and 17 depict the effects of carbon addition to an iron-cobalt alloy. FIGS. 18 and 19 depict the effects of titanium addition to an iron-cobalt alloy.

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FIG. 16 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for an iron-cobalt alloy with 5.63% by weight cobalt and 0.4% by weight manganese. Curve 260 depicts weight percentage of the ferrite phase. Curve 262 depicts

weight percentage of the austenite phase. The arrow points to the Curie temperature of the alloy. As shown in FIG. 16, the phase transformation was close to the Curie temperature but did not overlap with the Curie temperature for this alloy.

FIG. 17 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for an iron-cobalt alloy with 5.63% by weight cobalt, 0.4% by weight manganese, and 0.01% carbon. Curve 264 depicts weight percentage of the ferrite phase. Curve 266 depicts weight percentage of the austenite phase. The arrow points to the Curie temperature of the alloy. As shown in FIGS. 16 and 17, the phase transformation broadened with the addition of carbon to the alloy with the onset of the phase transformation shifting to a lower temperature.

Thus, carbon may be added to an iron alloy to lower the onset temperature and broaden the temperature range of the phase transformation.

FIG. 18 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for an iron-cobalt alloy with 5.63% by weight cobalt, 0.4% by weight manganese, and 0.085% carbon. Curve 268 depicts weight percentage of the ferrite phase. Curve 270 depicts weight percentage of the austenite phase. The arrow points to the Curie temperature of the alloy. As shown in FIG. 18, the phase transformation overlapped with the Curie temperature.

FIG. 19 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for an iron-cobalt alloy with 5.63% by weight cobalt, 0.4% by weight manganese, 0.085% carbon, and 0.4% titanium. Curve 272 depicts weight percentage of the ferrite phase. Curve 274 depicts weight percentage of the austenite phase. The arrow points to the Curie temperature of the alloy. As shown in FIGS. 18 and 19, the phase transformation narrowed with the addition of titanium to the alloy with the onset of the phase transformation shifting to a higher temperature. Thus, titanium may be added to an iron alloy to raise the onset temperature and narrow the temperature range of the phase transformation.

FIG. 20 depicts experimental calculations of weight percentages of ferrite and austenite phases versus temperature for 410 stainless steel type alloy (12% by weight chromium, 0.1% by weight carbon, 0.5% by weight manganese, 0.5% by weight silicon, with the balance being iron). Curve 276 depicts weight percentage of the ferrite phase. Curve 278 depicts weight percentage of the austenite phase. The arrow points to the Curie temperature of the alloy. As shown in FIG. 20, the Curie temperature is reduced with the addition of chromium.

Calculations for the Curie temperature and the phase transformation behavior were done for various mixtures of cobalt, carbon, manganese, silicon, vanadium, chromium, and titanium using the computational thermodynamic software (ThermoCalc and JMatPro) to predict the effect of additional elements on Curie Temperature ( $T_c$ ) for selected compositions and the temperature ( $A_1$ ) at which ferrite transforms to paramagnetic austenite. An equilibrium calculation temperature of 700 °C was used in all calculations. As shown in TABLE 3, as the weight percentage of cobalt

in the composition increased,  $T_c$  increased and  $A_1$  decreased. As shown in TABLE 3, addition of vanadium and/or titanium increased  $A_1$ . The addition of vanadium may allow increased amounts of chromium to be used in Curie heaters.

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TABLE 3

Composition (% by weight, balance being Fe)							Calculation Results	
Co	Cr	C	Mn	Si	V	Ti	$T_c$ (EC)	$A_1$ (EC)
0	12	0.1	0.5	0.5	0	0	723	814
2	12	0.1	0.5	0.5	0	0	739	800
4	12	0.1	0.5	0.5	0	0	754	788
6	12	0.1	0.5	0.5	0	0	769	780
8	12	0.1	0.5	0.5	0	0	783	773
10	12	0.1	0.5	0.5	0	0	797	766
0	12	0.1	0.5	0.5	1	0	726	
2	12	0.1	0.5	0.5	1	0	741	
4	12	0.1	0.5	0.5	1	0	756	
6	12	0.1	0.5	0.5	1	0	770	
8	12	0.1	0.5	0.5	1	0	784	794
10	12	0.1	0.5	0.5	1	0	797	
0	12	0.1	0.5	0.5	2	0	726	
2	12	0.1	0.5	0.5	2	0	742	
6	12	0.1	0.5	0.5	2	0	772	
8	12	0.1	0.5	0.5	2	0	785	817
10	12	0.1	0.5	0.5	2	0	797	
0	12	0.1	0.5	0.5	0	0.5	718	863
2	12	0.1	0.5	0.5	0	0.5	733	825
4	12	0.1	0.5	0.5	0	0.5	747	803
6	12	0.1	0.5	0.5	0	0.5	761	787
8	12	0.1	0.5	0.5	0	0.5	775	775
10	12	0.1	0.5	0.5	0	0.5	788	767
0	12	0.1	0.5	0.5	1	0.5	721	

Composition (% by weight, balance being Fe)							Calculation Results	
Co	Cr	C	Mn	Si	V	Ti	T <sub>c</sub> (EC)	A <sub>1</sub> (EC)
2	12	0.1	0.5	0.5	1	0.5	736	
4	12	0.1	0.5	0.5	1	0.5	750	
6	12	0.1	0.5	0.5	1	0.5	763	
8	12	0.1	0.5	0.5	1	0.5	776	
10	12	0.1	0.5	0.5	1	0.5	788	
0	12	0.1	0.5	0.5	2	0.5	725	
2	12	0.1	0.5	0.5	2	0.5	738	
4	12	0.1	0.5	0.5	2	0.5	752	
6	12	0.1	0.5	0.5	2	0.5	764	
8	12	0.1	0.5	0.5	2	0.5	777	
10	12	0.1	0.5	0.5	2	0.5	788	
0	12	0.1	0.5	0.5	0	1	712	>1000
2	12	0.1	0.5	0.5	0	1	727	877
4	12	0.1	0.5	0.5	0	1	741	836
6	12	0.1	0.5	0.5	0	1	755	810
8	12	0.1	0.5	0.5	0	1	768	794
10	12	0.1	0.5	0.5	0	1	781	780
0	12	0.1	0.5	0.5	1	1	715	
2	12	0.1	0.5	0.5	1	1	730	
4	12	0.1	0.5	0.5	1	1	743	
6	12	0.1	0.5	0.5	1	1	757	
8	12	0.1	0.5	0.5	1	1	770	821
10	12	0.1	0.5	0.5	1	1	782	
0	12	0.1	0.5	0.5	2	1	718	
2	12	0.1	0.5	0.5	2	1	732	
4	12	0.1	0.5	0.5	2	1	745	
6	12	0.1	0.5	0.5	2	1	758	
8	12	0.1	0.5	0.5	2	1	770	873



Composition (% by weight, balance being Fe)							Calculation Results	
Co	Cr	C	Mn	Si	V	Ti	T <sub>c</sub> (EC)	A <sub>1</sub> (EC)
10	12	0.1	0.5	0.5	2	1	782	
0	12	0.1	0.3	0.5	0	0	727	826
2	12	0.1	0.3	0.5	0	0	742	810
4	12	0.1	0.3	0.5	0	0	758	800
6	12	0.1	0.3	0.5	0	0	772	791
8	12	0.1	0.3	0.5	0	0	786	784
10	12	0.1	0.3	0.5	0	0	800	777
0	12	0.1	0.3	0.5	1	0	730	
2	12	0.1	0.3	0.5	1	0	745	
4	12	0.1	0.3	0.5	1	0	760	
6	12	0.1	0.3	0.5	1	0	774	
8	12	0.1	0.3	0.5	1	0	787	
10	12	0.1	0.3	0.5	1	0	801	
0	12	0.1	0.3	0.5	2	0	730	
2	12	0.1	0.3	0.5	2	0	746	
4	12	0.1	0.3	0.5	2	0	762	
6	12	0.1	0.3	0.5	2	0	775	
8	12	0.1	0.3	0.5	2	0	788	
10	12	0.1	0.3	0.5	2	0	801	
0	12	0.1	0.3	0.5	0	0.5	722	
2	12	0.1	0.3	0.5	0	0.5	737	
4	12	0.1	0.3	0.5	0	0.5	751	
6	12	0.1	0.3	0.5	0	0.5	765	
8	12	0.1	0.3	0.5	0	0.5	779	
10	12	0.1	0.3	0.5	0	0.5	792	
0	12	0.1	0.3	0.5	1	0.5	725	
2	12	0.1	0.3	0.5	1	0.5	740	
4	12	0.1	0.3	0.5	1	0.5	753	

Composition (% by weight, balance being Fe)							Calculation Results	
Co	Cr	C	Mn	Si	V	Ti	T <sub>c</sub> (EC)	A <sub>1</sub> (EC)
6	12	0.1	0.3	0.5	1	0.5	767	
8	12	0.1	0.3	0.5	1	0.5	780	
10	12	0.1	0.3	0.5	1	0.5	792	
0	12	0.1	0.3	0.5	2	0.5	728	
2	12	0.1	0.3	0.5	2	0.5	742	
4	12	0.1	0.3	0.5	2	0.5	755	
6	12	0.1	0.3	0.5	2	0.5	768	
8	12	0.1	0.3	0.5	2	0.5	780	
10	12	0.1	0.3	0.5	2	0.5	792	
0	12	0.1	0.3	0.5	0	1	715	
2	12	0.1	0.3	0.5	0	1	730	
4	12	0.1	0.3	0.5	0	1	745	
6	12	0.1	0.3	0.5	0	1	759	
8	12	0.1	0.3	0.5	0	1	772	
10	12	0.1	0.3	0.5	0	1	785	
0	12	0.1	0.3	0.5	1	1	719	
2	12	0.1	0.3	0.5	1	1	733	
4	12	0.1	0.3	0.5	1	1	747	
6	12	0.1	0.3	0.5	1	1	760	
8	12	0.1	0.3	0.5	1	1	773	834
10	12	0.1	0.3	0.5	1	1	786	
0	12	0.1	0.3	0.5	2	1	722	
2	12	0.1	0.3	0.5	2	1	736	
4	12	0.1	0.3	0.5	2	1	749	
6	12	0.1	0.3	0.5	2	1	762	
8	12	0.1	0.3	0.5	2	1	774	886
10	12	0.1	0.3	0.5	2	1	786	
7.5	12.25	0.1	0.3	0.5	0	0	781	785

Composition (% by weight, balance being Fe)							Calculation Results	
Co	Cr	C	Mn	Si	V	Ti	T <sub>c</sub> (EC)	A <sub>1</sub> (EC)
8.0	12.25	0.1	0.3	0.5	0	0	785	783
8.5	12.25	0.1	0.3	0.5	0	0	788	781
9.0	12.25	0.1	0.3	0.5	0	0	792	779
9.5	12.25	0.1	0.3	0.5	0	0	795	778
10.0	12.25	0.1	0.3	0.5	0	0	798	776
6.0	12.25	0.1	0.5	0.5	0	0	767	780
6.5	12.25	0.1	0.5	0.5	0	0	771	778
7.0	12.25	0.1	0.5	0.5	0	0	774	776
7.5	12.25	0.1	0.5	0.5	0	0	778	774
7.5	12.25	0.1	0.3	0.5	1	0	782	812
8.0	12.25	0.1	0.3	0.5	1	0	786	809
8.5	12.25	0.1	0.3	0.5	1	0	789	806
9.0	12.25	0.1	0.3	0.5	1	0	792	804
9.5	12.25	0.1	0.3	0.5	1	0	795	801
10.0	12.25	0.1	0.3	0.5	1	0	799	799
7.5	12.25	0.1	0.5	0.5	1	0	779	801
8.0	12.25	0.1	0.5	0.5	1	0	782	799
8.5	12.25	0.1	0.5	0.5	1	0	785	796
9.0	12.25	0.1	0.5	0.5	1	0	788	793
9.5	12.25	0.1	0.5	0.5	1	0	792	791
10.0	12.25	0.1	0.5	0.5	1	0	795	788
7.5	12.25	0.1	0.3	0.5	0	0.5	774	788
8.0	12.25	0.1	0.3	0.5	0	0.5	777	785
8.5	12.25	0.1	0.3	0.5	0	0.5	781	782
9.0	12.25	0.1	0.3	0.5	0	0.5	784	780
7.5	12.25	0.1	0.5	0.5	0	0.5	770	777
8.0	12.25	0.1	0.5	0.5	0	0.5	774	774
8.5	12.25	0.1	0.5	0.5	0	0.5	777	771

Composition (% by weight, balance being Fe)							Calculation Results	
Co	Cr	C	Mn	Si	V	Ti	T <sub>c</sub> (EC)	A <sub>1</sub> (EC)
7.5	12.25	0.1	0.3	0.5	1	0.5	775	823
8.0	12.25	0.1	0.3	0.5	1	0.5	778	819
8.5	12.25	0.1	0.3	0.5	1	0.5	782	814
9.0	12.25	0.1	0.3	0.5	1	0.5	785	810
9.5	12.25	0.1	0.3	0.5	1	0.5	788	807
10.0	12.25	0.1	0.3	0.5	1	0.5	791	803
10.5	12.25	0.1	0.3	0.5	1	0.5	794	800
11.0	12.25	0.1	0.3	0.5	1	0.5	797	797
7.5	12.25	0.1	0.5	0.5	1	0.5	771	811
8.0	12.25	0.1	0.5	0.5	1	0.5	775	807
8.5	12.25	0.1	0.5	0.5	1	0.5	778	803
9.0	12.25	0.1	0.5	0.5	1	0.5	781	799
9.5	12.25	0.1	0.5	0.5	1	0.5	784	796
10.0	12.25	0.1	0.5	0.5	1	0.5	787	792
10.5	12.25	0.1	0.5	0.5	1	0.5	790	789

Several iron-chromium alloys were prepared and their compositions are given in TABLE 4.

These cast alloys were processed into rods and wire, and the calculated and measured T<sub>c</sub> using a

5 torus technique is listed, along with calorimetry measurements.

TABLE 4

Alloy Designation	Actual Composition (% by weight, balance Fe)							T <sub>C</sub> (EC) (torus)	T <sub>C</sub> (EC) (calorimetry)	T <sub>C</sub> (EC) (calculated)	A <sub>1</sub> (EC) (calculated)
	Co	Cr	C	Mn	Si	V	Ti				
TC1b	0.02	13.2	0.08	0.45	0.69	0	0.01	692	--	717	819
TC2	2.44	12.3	0.10	0.48	0.47	0	0.01	--	--	742	793
TC3	4.81	12.3	0.10	0.48	0.46	0	0.01	--	--	761	783
TC4	9.75	12.2	0.07	0.49	0.47	0	0.01	759/ 682*	--	793	765
TC5	9.80	12.2	0.10	0.48	0.46	1.02	0.01	--	--	795	790
TC6	7.32	12.3	0.12	0.29	0.46	0.89	0.46	754	752	775	813
TC7	7.46	12.1	0.11	0.27	0.46	0.92	0	747	757	785	811
TC8	7.49	12.1	0.11	0.28	0.45	0	0	761	774	784	786

\* Two values represent T<sub>C</sub> during heating and T<sub>C</sub> during subsequent cooling.

Further modifications and alternative embodiments of various aspects of the invention may be apparent to those skilled in the art in view of this description. Accordingly, this description is to be construed as illustrative only and is for the purpose of teaching those skilled in the art the general manner of carrying out the invention. It is to be understood that the forms of the invention shown and described herein are to be taken as the presently preferred embodiments. Elements and materials may be substituted for those illustrated and described herein, parts and processes may be reversed, and certain features of the invention may be utilized independently, all as would be apparent to one skilled in the art after having the benefit of this description of the invention. Changes may be made in the elements described herein without departing from the spirit and scope of the invention as described in the following claims. In addition, it is to be understood that features described herein independently may, in certain embodiments, be combined.

CLAIMS

1. A heater, comprising:  
a heater section comprising iron, cobalt, and carbon;  
5 wherein the heater section has a Curie temperature ( $T_c$ ) less than a phase transformation temperature, and the  $T_c$  is at least 740 °C; and  
wherein the heater section is configured to provide, when time varying current is applied to the heater section, an electrical resistance.
2. The heater of claim 1, wherein the heater section further comprises one or more metals  
10 capable of forming carbides, and wherein at least one of the metals is vanadium and/or titanium.
3. The heater of any of claims 1 or 2, wherein the heater section further comprises manganese, nickel, silicon, chromium, and/or combinations thereof.
4. The heater of any of claims 1-3, wherein the content of iron in the heater section is at least 50% by weight.
- 15 5. The heater of any of claims 1-4, wherein the content of cobalt in the heater section is at least 2% by weight.
6. The heater of any of claims 1-5, wherein the heater section has at most 1% by weight of manganese, at most 1% by weight of nickel, at most 1% by weight of silicon, at most 1% by weight of vanadium, at most 1% by weight of titanium, and/or at most 1% by weight of manganese.
- 20 7. The heater of any of claims 1-6, wherein the heater section has at least 50% by weight iron, at least 6% by weight cobalt, at least 9% by weight chromium, and at least 0.5% by weight vanadium.
8. The heater of any of claims 1-7, wherein the heater section is configured to provide a reduced amount of heat at or near, and above, the Curie temperature.
- 25 9. The heater of any of claims 1-8, wherein the heater is located in a subsurface formation.
10. The heater of any of claims 1-9, wherein the heater is configured to provide heat to a subsurface formation.
11. The heater of any of claims 1-10, wherein the heater is configured to provide heat to a hydrocarbon containing formation such that at least some hydrocarbons in the formation are  
30 mobilized and/or pyrolyzed.
12. The heater of any of claims 1-11, wherein the heater section has a Curie temperature ( $T_c$ ) less than a phase transformation temperature, and the  $T_c$  is at least 800 °C.
13. The heater of any of claims 1-12, wherein the heater section has at least 50% by weight iron, at least 9% by weight chromium and at least 0.1% by weight carbon.
- 35 14. The heater of any of claims 1-13, wherein the content of chromium in the heater section is at least 11% by weight.

15. A method of heating a hydrocarbon containing formation using the heater as claimed in any of claims 1-14, the method comprising:

providing the heater to the formation; and

providing current to the heater such that the heater provides electrical resistance heating to at least a portion of the formation.

16. The method of claim 15, further comprising providing a reduced amount of heat at or near, and above, the Curie temperature.

17. The method of any of claims 15 or 16, further comprising providing heat to the formation such that at least some hydrocarbons in the formation are mobilized and/or pyrolyzed.

18. The method of any of claims 15-17, further comprising producing a fluid from the formation.

19. A composition comprising hydrocarbons produced from a subsurface formation using the heater as claimed in any of claims 1-14, or using the methods as claimed in any of claims 15-18.

20. A transportation fuel comprising hydrocarbons made from the composition as claimed in claim 19.

15

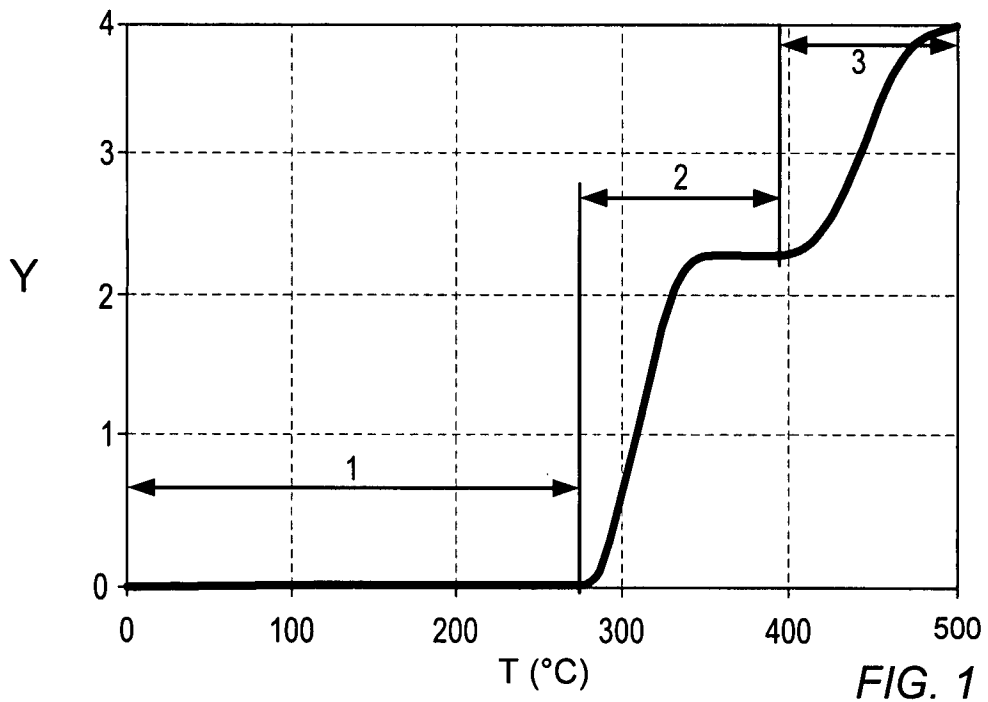


FIG. 1

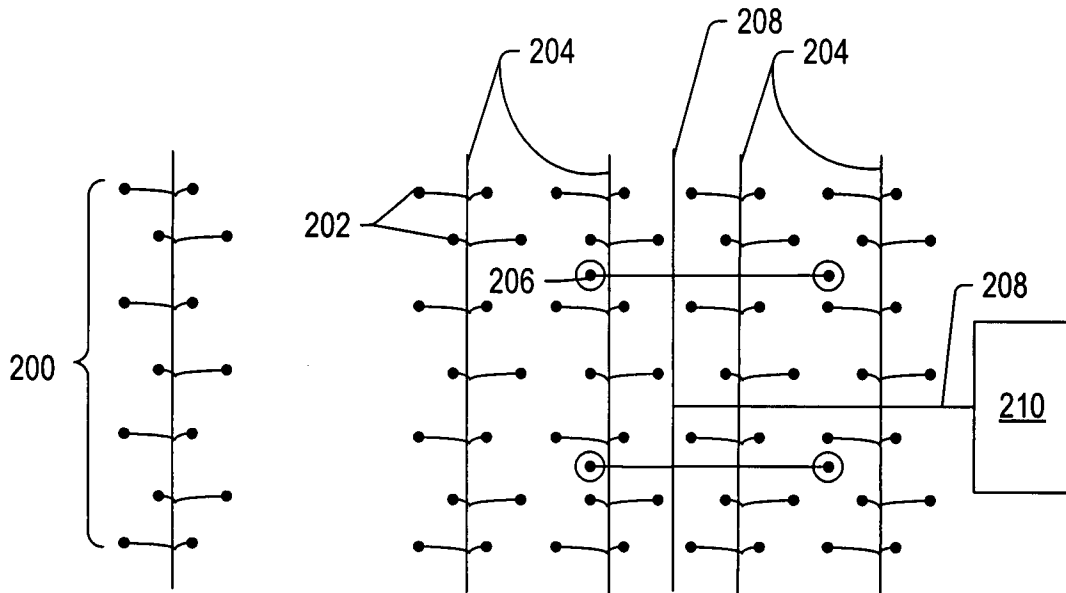


FIG. 2



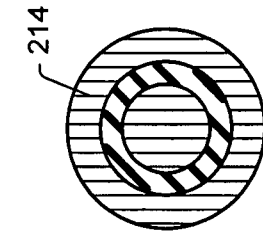


FIG. 5

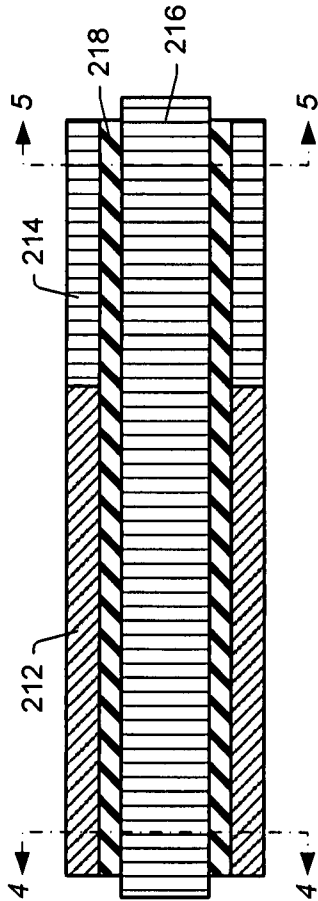


FIG. 3

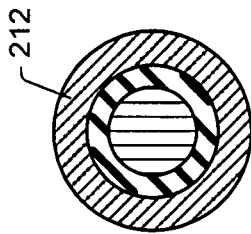


FIG. 4

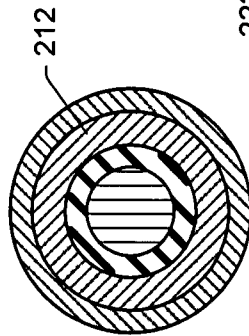


FIG. 7

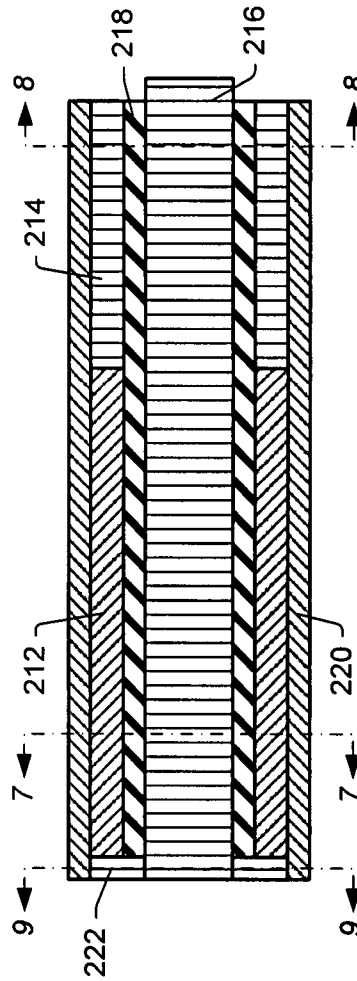


FIG. 6

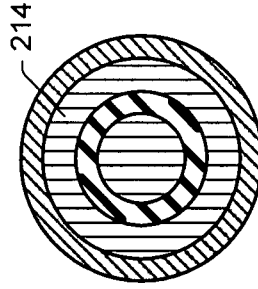


FIG. 8

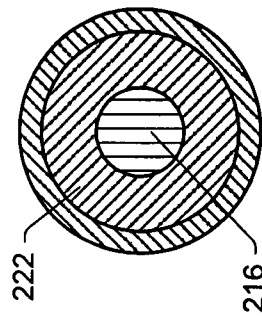


FIG. 9

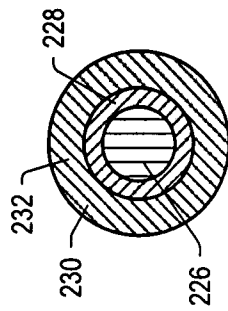


FIG. 10

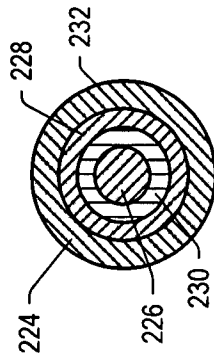


FIG. 11

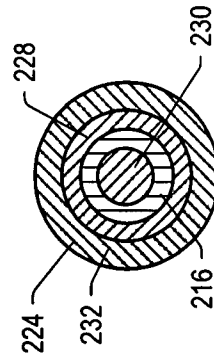


FIG. 12

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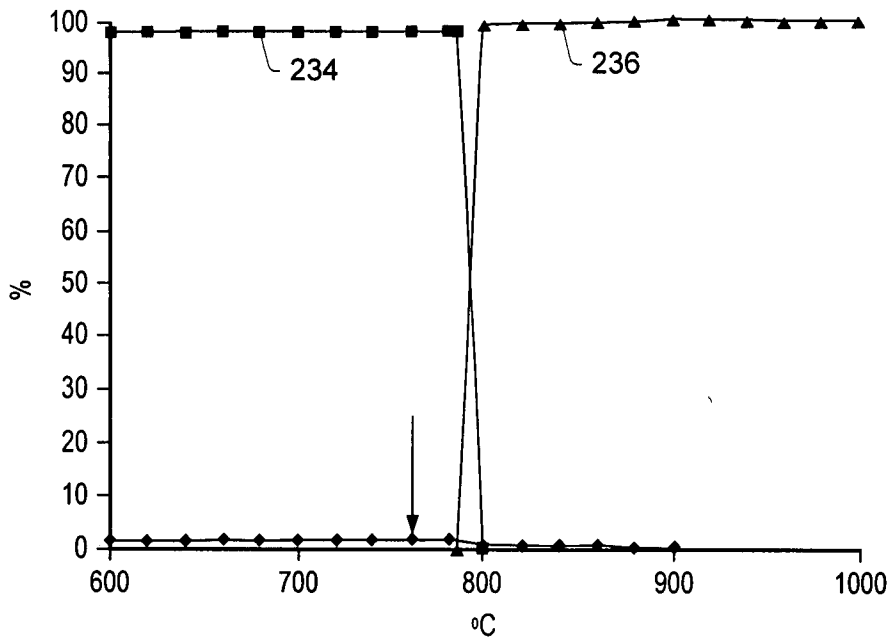


FIG. 13

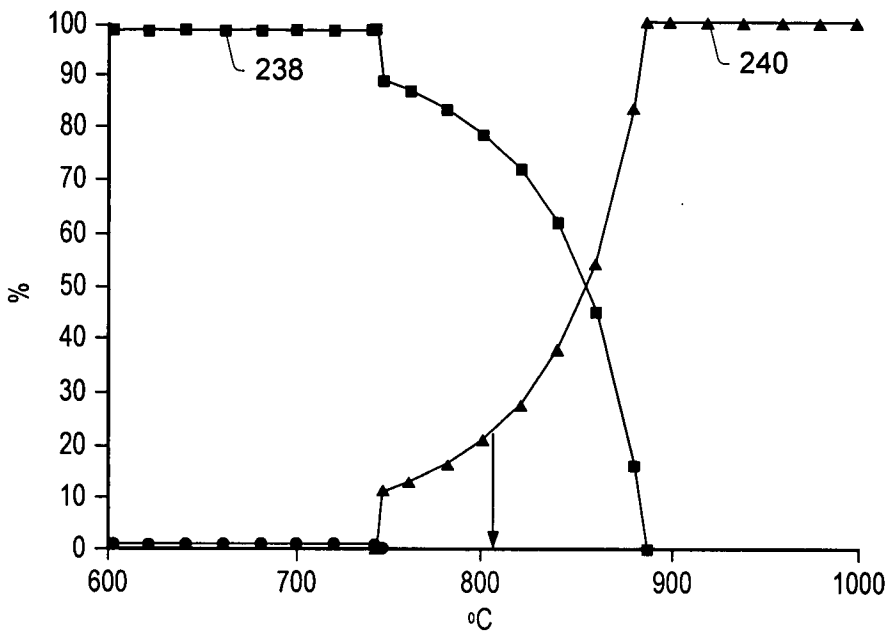


FIG. 14

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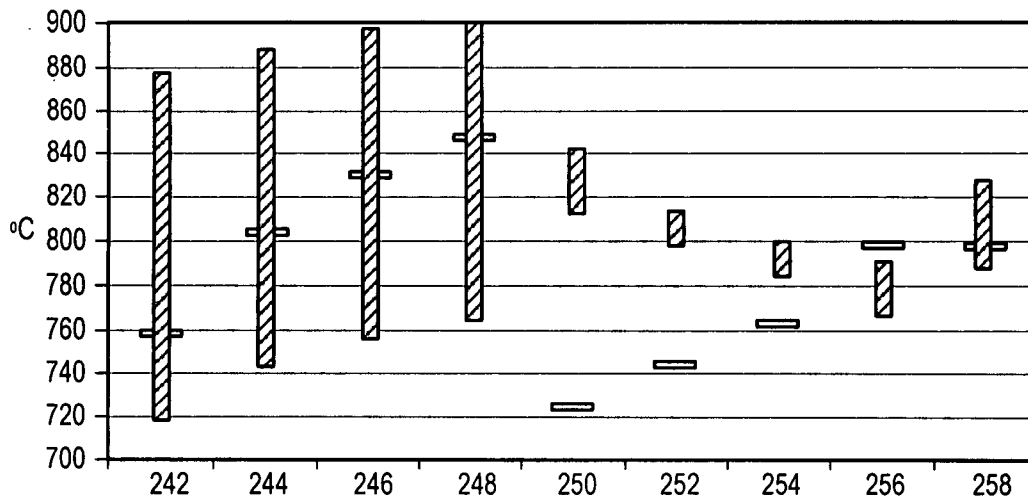


FIG. 15

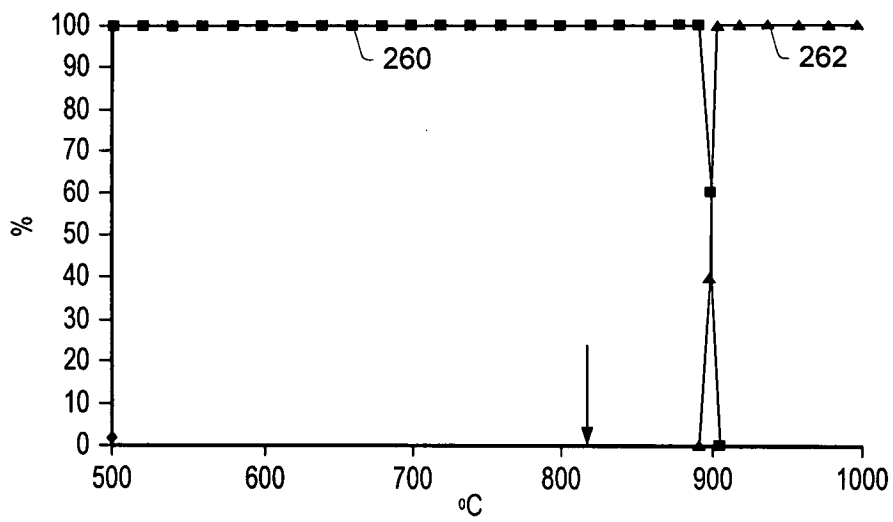


FIG. 16

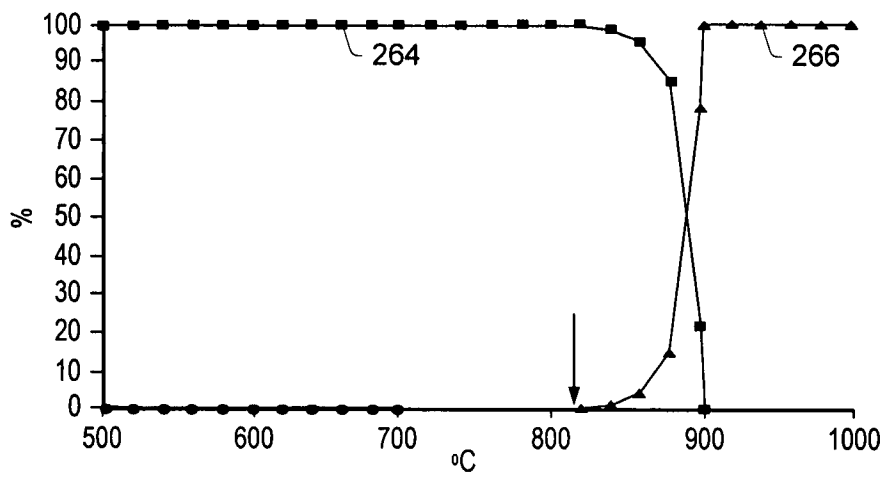


FIG. 17

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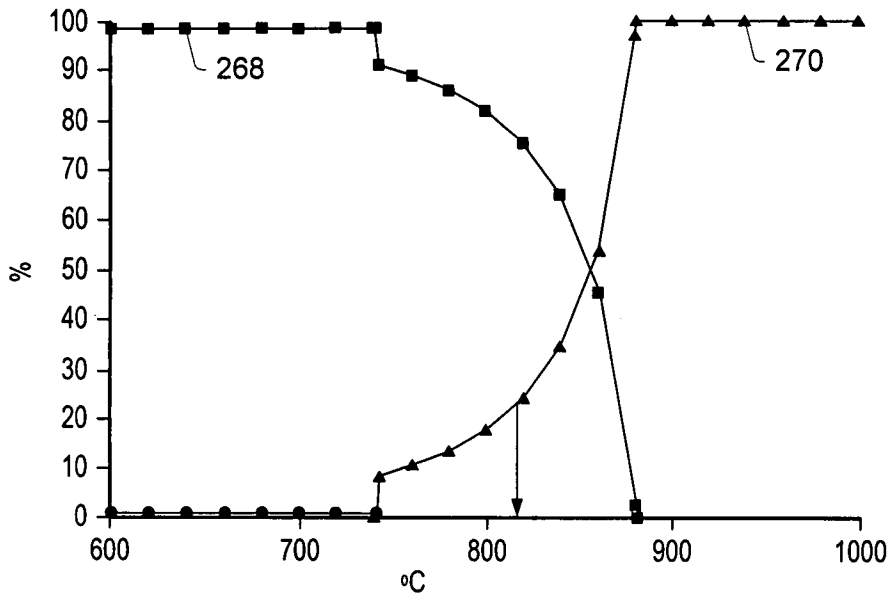


FIG. 18

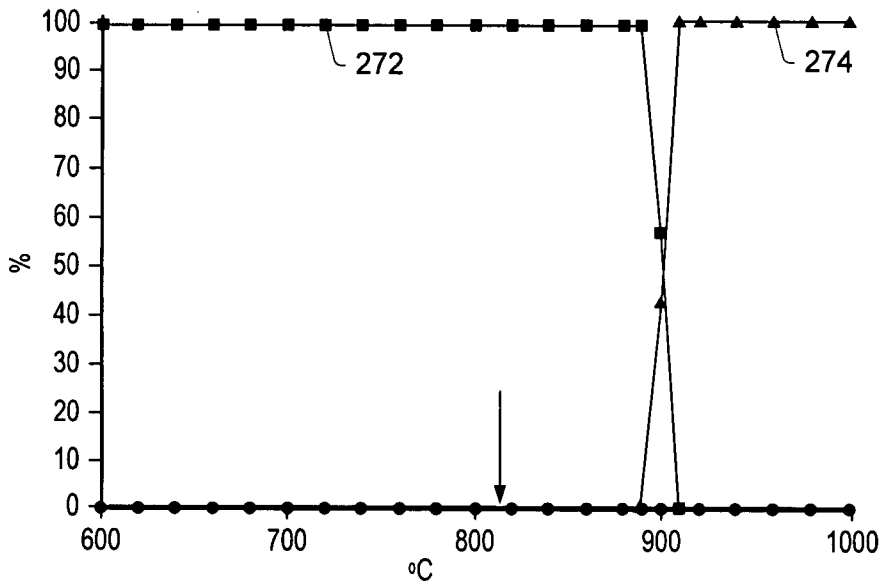


FIG. 19

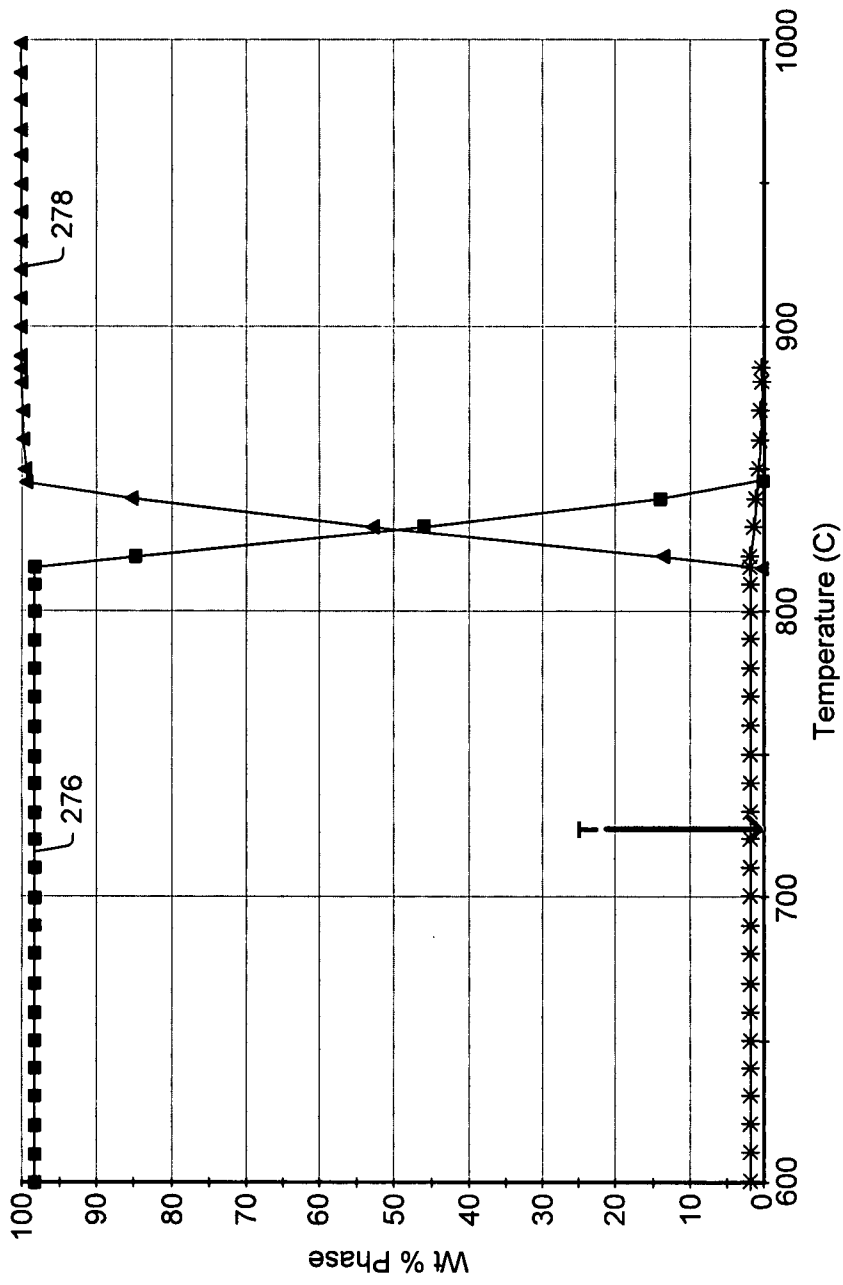


FIG. 20