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(54) **Titre : SYSTEMES ET PROCEDES DE CHAUFFAGE UTILISANT DES ALLIAGES A HAUTE RESISTANCE**
 (54) **Title: HEATING SYSTEMS AND METHODS USING HIGH STRENGTH ALLOYS**

(57) **Abrégé/Abstract:**

High strength metal alloys are described. At least one composition of a metal alloy includes chromium, nickel, copper, manganese, silicon, niobium, tungsten and iron. A heater system may include a canister at least partially made from material containing at least one of the metal alloys. A system for heating a subterranean formation may include a tubular that is at least partially made from a material containing at least one of the metal alloys.

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(54) Title: HIGH STRENGTH ALLOYS

(57) Abstract: High strength metal alloys are described. At least one composition of a metal alloy includes chromium, nickel, copper, manganese, silicon, niobium, tungsten and iron. A heater system may include a canister at least partially made from material containing at least one of the metal alloys. A system for heating a subterranean formation may include a tubular that is at least partially made from a material containing at least one of the metal alloys.

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HEATING SYSTEMS AND METHODS USING HIGH STRENGTH ALLOYS

BACKGROUND**1. Field of the Invention**

The present invention relates generally to metal compositions. In particular, the invention relates to metal alloys having high strength at high temperatures and/or low temperatures.

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.

A wellbore may be formed in a formation. In some embodiments, a casing or other pipe system may be placed or formed in a wellbore. In some embodiments, an expandable tubular may be used in a wellbore. Heaters may be placed in wellbores to heat a formation during an in situ process.

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 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.

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 Nos. 2,548,360 to Germain; 4,716,960 to Eastlund et al.; 4,716,960 to Eastlund et al.; and 5,065,818 to Van Egmond describes an electric heating element placed in a wellbore. U.S. Patent No. 6,023,554 to Vinegar et al. describes an electric heating element that is positioned in a casing. The heating element generates radiant energy that heats the casing.

U.S. Patent No. 4,570,715 to Van Meurs et al. describes an electric heating element. The heating element has an electrically conductive core, a surrounding layer of insulating material, and a surrounding metallic sheath. The conductive core may have a relatively low resistance at high temperatures. The insulating material may have electrical resistance, compressive strength, and heat conductivity properties that are relatively high at high temperatures. The insulating layer may inhibit arcing from the core to the metallic sheath. The metallic sheath may have tensile strength and creep resistance properties that are relatively high at high temperatures. U.S. Patent No. 5,060,287 to Van Egmond describes an electrical heating element having a copper-nickel alloy core.

Heaters may be manufactured from wrought stainless steels. U.S. Patent No. 7,153,373 to Maziasz et al. and U.S. Patent Application Publication No. US 2004/0191109 to Maziasz et al. described modified 237 stainless steels as cast microstructures or fined grained sheets and foils.

As outlined above, there has been a significant amount of effort to develop heaters, methods and systems to economically produce hydrocarbons, hydrogen, and/or other products from hydrocarbon containing formations. At present, however, there are still many hydrocarbon containing formations from which hydrocarbons, hydrogen, and/or other products cannot be economically produced. Thus, there is still a need for improved

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metals for heaters to be used in methods and systems for production of hydrocarbons, hydrogen, and/or other products from various hydrocarbon containing formations.

SUMMARY

Embodiments described herein generally relate to one or more metal compositions. In some embodiments, systems and methods using materials containing the metal compositions are described.

In some embodiments a metal alloy composition may include from 18 percent to 22 percent by weight chromium; from 5 percent to 13 percent by weight nickel; between 3 percent and 10 percent by weight copper; from 1 percent to 10 percent by weight manganese; from 0.3 percent to 1 percent by weight silicon; from 0.5 percent to 1.5 percent by weight niobium; from 0.5 to 2 percent by weight tungsten; and from 38 percent to 63 percent by weight iron.

In some embodiments, a metal alloy composition may include from 18 percent to 22 percent by weight chromium; from 5 percent to 9 percent by weight nickel; from 1 percent to 6 percent by weight copper; from 0.5 percent to 1.5 percent by weight niobium; from 1 to 10 percent by weight manganese; from 0.5 to 1.5 percent by weight of tungsten; from 36 percent to 74 percent by weight iron; and precipitates of nanonitrides, wherein the ratio of tungsten to copper is between about 1/10 and 10/1.

In some embodiments, the invention describes a heater system may include a heat generating element and a canister surrounding the heat generating element least partially made from material containing: from 18 percent to 22 percent by weight chromium; from 5 percent to 14 percent by weight nickel; from 1 percent to 10 percent by weight copper; from 0.5 percent to 1.5 percent by weight niobium; from 36 percent to 70.5 percent by weight iron; and precipitates of nanonitrides.

In some embodiments, the invention describes a system for heating a subterranean formation comprising a tubular, the tubular at least partially made from a material containing: from 18 percent to 22 percent by weight chromium; from 10 percent to 14 percent by weight nickel; from 1 percent to 10 percent by weight copper; from 0.5 percent to 1.5 percent by weight niobium; from 36 percent to 70.5 percent by weight iron; and precipitates of nanonitrides.

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According to another aspect of the present invention, there is provided a heater system comprising: a heat generating element; and a canister surrounding the heat generating element, wherein the canister is at least partially made of a material comprising: from 18 percent to 22 percent by weight chromium; from 5 percent to 14 percent by weight nickel; from 1 percent to 10 percent by weight copper; from 0.5 percent to 1.5 percent by weight niobium; from 36 percent to 70.5 percent by weight iron; from 1 percent to 10 percent by weight manganese; from 0.12 percent to about 0.5 percent by weight nitrogen; and from about 0.08 percent to about 0.2 percent by weight carbon; wherein the composition, when at 800 °C, has at least two percent by weight of precipitates comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N) or M₂₃C₆ phases, where M is nickel, copper, niobium, iron or manganese, wherein the precipitates comprise nanonitrides, the nanonitrides comprising particles having dimensions in the range of five to one hundred nanometers.

According to still another aspect of the present invention, there is provided a system for heating a subterranean formation comprising a tubular, the tubular at least partially made from a material comprising: from 18 percent to 22 percent by weight chromium; from 10 percent to 14 percent by weight nickel; from 1 percent to 10 percent by weight copper; from 0.5 percent to 1.5 percent by weight niobium; from 36 percent to 70.5 percent by weight iron; from 1 percent to 10 percent by weight manganese; from 0.12 percent to about 0.5 percent by weight nitrogen; and from about 0.08 percent to about 0.2 percent by weight carbon; wherein the composition, when at 800 °C, has at least two percent by weight of precipitates comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N) or M₂₃C₆ phases, where M is nickel, copper, niobium, iron or manganese, wherein the precipitates comprise nanonitrides, the nanonitrides comprising particles having dimensions in the range of five to one hundred nanometers.

According to yet another aspect of the present invention, there is provided a method of heating a subterranean formation comprising: positioning one or more heater systems in a subterranean formation, wherein at least one of the heater systems comprises: a heat generating element; and a canister surrounding the heat generating element, wherein the canister is at least partially made of a material comprising: from about 18 percent to about 22 percent by weight chromium; from about 5 percent to about 14 percent by weight

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nickel; from about 1 percent to about 10 percent by weight copper; from above 0.5 percent to about 1.5 percent by weight niobium; from about 36 percent to about 70.5 percent by weight iron; from 1 percent to 10 percent by weight manganese; from 0.12 percent to about 0.5 percent by weight nitrogen; from about 0.08 percent to about 0.2 percent by weight carbon; wherein the composition, when at 800 °C, has at least two percent by weight of precipitates comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N) or M₂₃C₆ phases, where M is nickel, copper, niobium, iron or manganese, wherein the precipitates comprise nanonitrides, the nanonitrides comprising particles having dimensions in the range of five to one hundred nanometers; and allowing heat from the heater system to heat at least a portion of the subterranean formation.

According to a further aspect of the present invention, there is provided a method of heating a subterranean formation, comprising: positioning one or more heater systems in a subterranean formation, wherein at least one of the heater systems comprises a tubular and at least a portion of the tubular is made from a material comprising: from about 18 percent to about 22 percent by weight chromium; from about 5 percent to about 14 percent by weight nickel; from about 1 percent to about 10 percent by weight copper; from above 0.5 percent to about 1.5 percent by weight niobium; from about 36 percent to about 70.5 percent by weight iron; from 1 percent to 10 percent by weight manganese; from 0.12 percent to about 0.5 percent by weight nitrogen; from about 0.08 percent to about 0.2 percent by weight carbon; wherein the composition, when at 800 °C, has at least two percent by weight of precipitates comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N) or M₂₃C₆ phases, where M is nickel, copper, niobium, iron or manganese, wherein the precipitates comprise nanonitrides, the nanonitrides comprising particles having dimensions in the range of five to one hundred nanometers; and allowing heat from the heater system to heat at least a portion of the subterranean formation.

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
5 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

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

15 FIG. 2 depicts experimental calculation of weight percentages of phases versus weight percentages of chromium in an alloy.

FIG. 3 depicts experimental calculation of weight percentages of phases versus weight percentages of silicon in an alloy.

20 FIG. 4 depicts experimental calculation of weight percentages of phases versus weight percentages of tungsten in an alloy.

FIG. 5 depicts experimental calculation of weight percentages of phases versus weight percentages of niobium in an alloy.

FIG. 6 depicts experimental calculation of weight percentages of phases versus weight percentages of carbon in an alloy.

25 FIG. 7 depicts experimental calculation of weight percentages of phases versus weight percentages of nitrogen in an alloy.

FIG. 8 depicts experimental calculation of weight percentages of phases versus weight percentages of titanium in an alloy.

30 FIG. 9 depicts experimental calculation of weight percentages of phases versus weight percentages of copper in an alloy.

FIG. 10 depicts experimental calculation of weight percentages of phases versus weight percentages of manganese in an alloy.

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FIG. 11 depicts experimental calculation of weight percentages of phases versus weight percentages of nickel in an alloy.

FIG. 12 depicts experimental calculation of weight percentages of phases versus weight percentages of molybdenum in an alloy.

FIG. 13 depicts yield strengths and ultimate tensile strengths for different metals.

FIG. 14 depicts yield strengths for different metals.

FIG. 15 depicts ultimate tensile strengths for different metals.

FIG. 16 depicts yield strengths for different metals.

FIG. 17 depicts ultimate tensile strengths for different metals.

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 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.

“API gravity” refers to API gravity at 15.5 °C (60 °F). API gravity is as determined by ASTM Method D6822.

“Bare metal” and “exposed metal” refer to metals of elongated members that do not include a layer of electrical insulation, such as mineral insulation, that is designed to provide electrical insulation for the metal throughout an operating temperature range of the elongated member. Bare metal and exposed metal may encompass a metal that includes a corrosion inhibitor such as a naturally occurring oxidation layer, an applied oxidation layer, and/or a film. Bare metal and exposed metal include metals with polymeric or other types

of electrical insulation that cannot retain electrical insulating properties at typical operating temperature of the elongated member. Such material may be placed on the metal and may be thermally degraded during use of the heater.

“Carbon number” refers to the number of carbon atoms in a molecule. A hydrocarbon fluid may include various hydrocarbons with different carbon numbers. The hydrocarbon fluid may be described by a carbon number distribution. Carbon numbers and/or carbon number distributions may be determined by true boiling point distribution and/or gas-liquid chromatography.

“Column X element” or “Column X elements” refer to one or more elements of Column X of the Periodic Table, and/or one or more compounds of one or more elements of Column X of the Periodic Table, in which X corresponds to a column number (for example, 13-18) of the Periodic Table. For example, “Column 15 elements” refer to elements from Column 15 of the Periodic Table and/or compounds of one or more elements from Column 15 of the Periodic Table.

“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 Curie temperature, the ferromagnetic material begins to lose its ferromagnetic properties when an increasing electrical current is passed through the ferromagnetic material.

“Fluid pressure” is a pressure generated by a fluid in a formation. “Lithostatic pressure” (sometimes referred to as “lithostatic stress”) is a pressure in a formation equal to a weight per unit area of an overlying rock mass. “Hydrostatic pressure” is a pressure in a formation exerted by a column of water.

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 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 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.

5 “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
10 removed from the formation.

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
15 heat by burning a fuel external to or in a formation. The systems may be surface burners, downhole gas burners, flameless 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
20 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 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,
25 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.

A “heater” is any system or heat source for generating heat in a well or a near
30 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.

“Heavy hydrocarbons” are viscous hydrocarbon fluids. Heavy hydrocarbons may include highly viscous hydrocarbon fluids such as heavy oil, tar, and/or asphalt. Heavy hydrocarbons may include carbon and hydrogen, as well as smaller concentrations of sulfur, oxygen, and nitrogen. Additional elements may also be present in heavy hydrocarbons in trace amounts. Heavy hydrocarbons may be classified by API gravity. Heavy hydrocarbons generally have an API gravity below 20°. Heavy oil, for example, generally has an API gravity of 10-20°, whereas tar generally has an API gravity below 10°. The viscosity of heavy hydrocarbons is generally greater than 100 centipoise at 15 °C. Heavy hydrocarbons may include aromatics or other complex ring hydrocarbons.

Heavy hydrocarbons may be found in a relatively permeable formation. The relatively permeable formation may include heavy hydrocarbons entrained in, for example, sand or carbonate. “Relatively permeable” is defined, with respect to formations or portions thereof, as an average permeability of 10 millidarcy or more (for example, 10 or 100 millidarcy). “Relatively low permeability” is defined, with respect to formations or portions thereof, as an average permeability of less than 10 millidarcy. One darcy is equal to 0.99 square micrometers. An impermeable layer generally has a permeability of less than 0.1 millidarcy.

Certain types of formations that include heavy hydrocarbons may also be, but are not limited to, natural mineral waxes, or natural asphaltites. “Natural mineral waxes” typically occur in substantially tubular veins that may be several meters wide, several kilometers long, and hundreds of meters deep. “Natural asphaltites” include solid hydrocarbons of an aromatic composition and typically occur in large veins. In situ recovery of hydrocarbons from formations such as natural mineral waxes and natural asphaltites may include melting to form liquid hydrocarbons and/or solution mining of hydrocarbons from the formations.

“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, 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 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.

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.

“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.

“Kerogen” is a solid, insoluble hydrocarbon that has been converted by natural degradation and that principally contains carbon, hydrogen, nitrogen, oxygen, and sulfur. Coal and oil shale are typical examples of materials that contain kerogen. “Bitumen” is a non-crystalline solid or viscous hydrocarbon material that is substantially soluble in carbon disulfide. “Oil” is a fluid containing a mixture of condensable hydrocarbons.

“Modulated direct current (DC)” refers to any substantially non-sinusoidal time-varying current that produces skin effect electricity flow in a ferromagnetic conductor.

“Nitride” refers to a compound of nitrogen and one or more other elements of the Periodic Table. Nitrides include, but are not limited to, silicon nitride, boron nitride, or alumina nitride.

“Periodic Table” refers to the Periodic Table as specified by the International Union of Pure and Applied Chemistry (IUPAC), November 2003. In the scope of this application, weight of a metal from the Periodic Table, weight of a compound of a metal from the Periodic Table, weight of an element from the Periodic Table, or weight of a compound of an element from the Periodic Table is calculated as the weight of metal or the weight of element. For example, if 0.1 grams of MoO_3 is used per gram of catalyst, the calculated weight of the molybdenum metal in the catalyst is 0.067 grams per gram of catalyst.

“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.

“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.

“Subsidence” is a downward movement of a portion of a formation relative to an initial elevation of the surface.

“Tar” is a viscous hydrocarbon that generally has a viscosity greater than 10,000 centipoise at 15 °C. The specific gravity of tar generally is greater than 1.000. Tar may have an API gravity less than 10°.

A “tar sands formation” is a formation in which hydrocarbons are predominantly present in the form of heavy hydrocarbons and/or tar entrained in a mineral grain framework or other host lithology (for example, sand or carbonate). Examples of tar sands formations include formations such as the Athabasca formation, the Grosmont formation, and the Peace River formation, all three in Alberta, Canada; and the Faja formation in the Orinoco belt in Venezuela.

“Temperature limited heater” generally refers to a heater that regulates heat output (for example, reduces heat output) above a specified temperature without the use of external controls such as temperature controllers, power regulators, rectifiers, or other devices. Temperature limited heaters may be AC (alternating current) or modulated (for example, “chopped”) DC (direct current) powered electrical resistance heaters.

“Thermal conductivity” is a property of a material that describes the rate at which heat flows, in steady state, between two surfaces of the material for a given temperature difference between the two surfaces.

“Thermal fracture” refers to fractures created in a formation caused by expansion or contraction of a formation and/or fluids in the formation, which is in turn caused by increasing/decreasing the temperature of the formation and/or fluids in the formation, and/or by increasing/decreasing a pressure of fluids in the formation due to heating.

“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).

“Turndown ratio” for the temperature limited heater is the ratio of the highest AC or modulated DC resistance below the Curie temperature to the lowest resistance above the
5 Curie temperature for a given current.

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
10 “wellbore.”

FIG. 1 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
15 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. 1, the barrier
20 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
25 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
30 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.

When the formation is heated, the heat input into the formation may cause expansion of the formation and geomechanical motion. The heat sources turned on before, at the same time, or during a dewatering process. Computer simulations may model formation response to heating. The computer simulations may be used to develop a pattern and time sequence for activating heat sources in the formation so that geomechanical motion of the formation does not adversely affect the functionality of heat sources, production wells, and other equipment in the formation.

Heating the formation may cause an increase in permeability and/or porosity of the formation. Increases in permeability and/or porosity may result from a reduction of mass in the formation due to vaporization and removal of water, removal of hydrocarbons, and/or creation of fractures. Fluid may flow more easily in the heated portion of the formation because of the increased permeability and/or porosity of the formation. Fluid in the heated portion of the formation may move a considerable distance through the formation because of the increased permeability and/or porosity. The considerable distance may be over 1000 m depending on various factors, such as permeability of the formation, properties of the fluid, temperature of the formation, and pressure gradient allowing movement of the fluid. The ability of fluid to travel considerable distance in the formation allows production wells to be spaced relatively far apart in the formation.

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.

More than one heat source may be positioned in the production well. A heat source in a lower portion of the production well may be turned off when superposition of heat

from adjacent heat sources heats the formation sufficiently to counteract benefits provided by heating the formation with the production well. In some embodiments, the heat source in an upper portion of the production well may remain on after the heat source in the lower portion of the production well is deactivated. The heat source in the upper portion of the well may inhibit condensation and reflux of formation fluid.

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 (C6 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 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.

In some hydrocarbon containing formations, hydrocarbons in the formation may be heated to pyrolysis temperatures before substantial permeability has been generated in the heated portion of the formation. An initial lack of permeability may inhibit the transport of generated fluids to production wells 206. During initial heating, fluid pressure in the

formation may increase proximate heat sources 202. The increased fluid pressure may be released, monitored, altered, and/or controlled through one or more heat sources 202. For example, selected heat sources 202 or separate pressure relief wells may include pressure relief valves that allow for removal of some fluid from the formation.

5 In some embodiments, pressure generated by expansion of pyrolysis fluids or other fluids generated in the formation may be allowed to increase although an open path to production wells 206 or any other pressure sink may not yet exist in the formation. The fluid pressure may be allowed to increase towards a lithostatic pressure. Fractures in the hydrocarbon containing formation may form when the fluid approaches the lithostatic
10 pressure. For example, fractures may form from heat sources 202 to production wells 206 in the heated portion of the formation. The generation of fractures in the heated portion may relieve some of the pressure in the portion. Pressure in the formation may have to be maintained below a selected pressure to inhibit unwanted production, fracturing of the overburden or underburden, and/or coking of hydrocarbons in the formation.

15 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
20 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
25 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
30 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.

Generation of relatively low molecular weight hydrocarbons is believed to be due, in part, to autogenous generation and reaction of hydrogen in a portion of the hydrocarbon containing formation. For example, maintaining an increased pressure may force hydrogen generated during pyrolysis into the liquid phase within the formation. Heating the portion to a temperature in a pyrolysis temperature range may pyrolyze hydrocarbons in the formation to generate liquid phase pyrolyzation fluids. The generated liquid phase pyrolyzation fluids components may include double bonds and/or radicals. Hydrogen (H₂) in the liquid phase may reduce double bonds of the generated pyrolyzation fluids, thereby reducing a potential for polymerization or formation of long chain compounds from the generated pyrolyzation fluids. In addition, H₂ may also neutralize radicals in the generated pyrolyzation fluids. Therefore, H₂ in the liquid phase may inhibit the generated pyrolyzation fluids from reacting with each other and/or with other compounds in the formation.

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.

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 to provide a reduced amount of heat at or near the Curie temperature 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. In certain embodiments, the selected temperature is within 35 °C, within 25 °C, within 20 °C, or within 10 °C of the Curie temperature. 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 to exceed, a maximum operating temperature of the heater. Heat output from portions of a temperature limited heater approaching a Curie temperature 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 of an electrically resistive portion of the heater when the temperature limited heater is energized by a time-varying current. The first heat
5 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 50 °C, 75 °C, 100 °C, or 125 °C below the Curie temperature of the ferromagnetic material in the temperature limited heater.

The temperature limited heater may be energized by time-varying current
10 (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.

15 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
20 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, and 1000 or greater). As the temperature of the ferromagnetic material is raised above the Curie temperature and/or as the applied electrical current is increased, the magnetic permeability of the ferromagnetic material decreases substantially and the skin depth
25 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 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,
30 reach, or are above the Curie temperature may have reduced heat dissipation. Sections of the temperature limited heater that are not at or near the Curie temperature 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.; and U.S. Patent No. 4,849,611 to Whitney et al. describes a plurality of 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 in a desired range of temperature operation. Operation within the desired 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 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 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 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 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 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 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. 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 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 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 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 thermocouples on the heaters to monitor potential overheating at hot spots.

In some embodiments, temperature limited heaters are manufactured from austenitic stainless steels. These austenitic steels may include alloys with a face centered cubic (fcc) austenite phase being the primary phase. The fcc austenite phase may be stabilized by controlling the Fe-Cr-Ni and/or the Fe₁₈Cr₈-Ni concentration. Strength of the austenitic phase may be increased by incorporating other alloys in the fcc lattice. For low-temperature applications, the strength may be raised by adding alloying elements that increase the strength of the fcc lattice. This type of strengthening may be referred to as “solid solution strengthening”. As the use temperature is increased, however, alloying elements in the austenite phase may react to form new phases such as M₂₃C₆, where M includes chromium and other elements that can form carbides. Other phases may form in austenite containing elements from Columns 4-13 of the Periodic Table. Examples of such elements include, but are not limited to, niobium, titanium, vanadium, tungsten, aluminum, or mixtures thereof. The size and distribution of various phases and their stability in the desired use temperature range determines the mechanical properties of the stainless steel. Nano-scale dispersions of precipitates such as carbides may produce the highest strength at high temperatures, but due to the size of the carbides, they may become unstable and coarsen. Alloys containing nano-scale precipitate dispersions may be unstable at temperatures of at least 750 °C. Since, heaters may heat a subsurface formation to temperatures at least 700 °C, heaters having improved strength alloys capable of withstanding temperatures of at least 700 °C are desired.

In some embodiments, iron, chromium, and nickel alloys containing manganese, copper and tungsten, in combination with niobium, carbon and nitrogen, may maintain a finer grain size despite high temperature solution annealing or processing. Such behavior may be beneficial in reducing a heat-affected-zone in welded material. Higher solution-annealing temperatures are particularly important for achieving the best metal carbide (MC) nanocarbide. For example, niobium carbide nanocarbide strengthens during high-temperature creep service, and such effects are amplified (finer nanocarbide structures that are stable) by compositions of the improved alloys. Tubing and canister applications that include the composition of the improved alloys and are wrought processed result in stainless steels that may be able to age-harden during service at 700 °C to 800 °C. Improved alloys may be able to age-harden even more if the alloys are cold-strained prior to high-temperature service, but such cold-prestraining is not necessary for good high temperature properties or age-hardening. Some prior art alloys, such as NF709 require

cold-prestraining to achieve good high temperature creep properties, and this is a disadvantage in particular because after such alloys are welded, the advantages of the cold-prestraining in the weld heat effected zone are lost. Other prior art alloys are adversely effected by cold-prestraining with respect to high-temperature strength and long-term durability. Thus, cold prestraining may be limited or not permitted by, for example, construction codes.

In some embodiments of the new alloy compositions, the alloy may be cold worked by, for example, twenty percent, and the yield strength at 800 °C is not changed by more than twenty percent from yield strength at 800 °C of freshly annealed alloy.

The improved alloys described herein are suitable for low temperature applications, for example, cryogenic applications. The improved alloys which have strength and sufficient ductility at temperatures of, for example, -50 °C to -200 °C, also retain strength at higher temperatures than many alloys often used in cryogenic applications, such as 201LN and YUS130, thus for services such as liquefied natural gas, where a failure may result in a fire, the improved alloy would retain strength in the vicinity of the fire longer than other materials.

An improved alloy composition may include, by weight: 18% to 22% chromium, 5% to 13% nickel (and in some embodiments, from 5% to 9% by weight nickel), 1% to 10% copper (and in some embodiments, above 2% to 6% copper), 1% to 10% manganese, 0.3% to 1% silicon, 0.5% to 1.5% niobium, 0.5% to 2% tungsten, and with the balance being essentially iron (for example, 47.8% to 68.12% iron). The composition may, in some embodiments, include other components, for example, 0.3% to 1% molybdenum, 0.08% to 0.2% carbon, 0.2% to 0.5% nitrogen or mixtures thereof. Other impurities or minor components typically present in steels may also be present. Such an improved alloy may be useful when processed by hot deformation, cold deformation, and/or welding into, for example, casings, canisters, or strength members for heaters. In some embodiments, the improved alloy includes, by weight: 20% chromium, 3% copper, 4% manganese, 0.3% molybdenum, 0.77% niobium, 13% nickel, 0.5% silicon, 1% tungsten, 0.09% carbon, and 0.26% nitrogen, with the balance being essentially iron. In certain embodiments, the improved alloy includes, by weight: 19% chromium, 4.2% manganese, 0.3% molybdenum, 0.8% niobium, 12.5% nickel, 0.5% silicon, 0.09% carbon, 0.24% nitrogen by weight with the balance being essentially iron. In certain embodiments, the improved alloy includes, by weight: about 21% chromium, about 3% copper, about 8% manganese, about 0.3%

molybdenum, about 0.8% niobium, about 7% nickel, about 0.5% silicon, about 1% tungsten, about 0.13% carbon, and about 0.37% nitrogen, with the balance being essentially iron. In some embodiments, the improved alloy includes, by weight: 20% chromium, 4.4% copper, 4.5 % manganese, 0.3% molybdenum, 0.8% niobium, 7% nickel, 0.5% silicon, 1% tungsten, 0.24% carbon, 0.3% nitrogen by weight with the balance being essentially iron. In some embodiments, improved alloys may vary an amount of manganese, amount of nickel, a W/Cu ratio, a Mo/W ratio, a C/N ratio, a Mn/N ratio, a Mn/Nb ratio, a Mn/Si ratio and/or a Mn/Ni ratio to enhance resistance to high temperature sulfidation, increase high temperature strength, and/or reduce cost. For example, for the improved wrought alloys to have a stable parent austenite phase, high strength from 600 °C to 900 °C, and stable nano carbide and nanocarbonitride microstructures, the improved wrought alloys may include combinations of alloying elements present in the the improved wrought alloys such that the following ratios (using wt.%) are achieved: a) Mo/W – 0.3 to 0.5; b) W/Cu – 0.25 to 0.33; c) C/N – 0.25 to 0.33; d) Mn/Ni – 0.3 to 1.5; e) Mn/N – 20 to 25; f) Mn/Nb – 5 to 13; and g) Mn/Si – 4 to 20; and carbon plus nitrogen is from 0.3 wt% to 0.6 wt%.

Improved wrought alloy compositions may include the compositions described in the preceding paragraphs and compositions disclosed in U.S. Patent No. 7,153,373. The improved wrought alloy composition may include at least 3.25% by weight precipitates at 800 °C. The improved wrought alloy composition may have been processed by aging or hot working and/or by cold working. As a result of such aging or hot working and/or cold working, the improved wrought alloy compositions (for example, NbC, Cr-rich $M_{23}C_6$) may contain nanocarbonitrides precipitates. Such nanocarbonitride precipitates are not known to be present in cast compositions such as those disclosed in U.S. Patent No. 7,153,373, and are believed to form upon hot working and/or cold working of the compositions. The nanocarbonitride precipitates may include particles having dimensions from 5 nanometers to 100 nanometers, from 10 nanometers to 90 nanometers, or from 20 to 80 nanometers. These wrought alloys may have microstructures that include, but are not limited to, nanocarbides (for example, NbC, Cr-rich $M_{23}C_6$), which form during aging (stress-free) or creep (stress < 0.5 yield stress (YS)). The nanocarbide precipitates may include particles having dimensions from 5 nanometers to 100 nanometers, from 10 nanometers to 90 nanometers, or from 20 nanometers to 80 nanometers. The microstructures may be a consequence of both the native alloy composition and the details

of the wrought processing. In solution annealed material, the concentration of such nanoscale particles may be low. The nanoscale particles may be affected by solution anneal temperature/time (more and finer dispersion with longer anneal above 1150 °C) and by cold- or warm- prestrain (cold work) after the solution anneal treatment. Cold prestrain may create dislocation networks within the grains that may serve as nucleation sites for the nanocarbides. Solution annealed material initially has zero percent cold work. Bending, stretching, coiling, rolling or swaging may create, for example 5-15% cold work. The effect of the nanocarbides on yield strength or creep strength may be to provide strength based on dislocation-pinning, with more closely-spaced pinning sites (higher concentration, finer dispersion) providing more strength (particles are barriers to climb or glide of dislocations).

The improved wrought alloy may include nanonitrides (for example, niobium chromium nitrides (NbCrN)) in the matrix together with nanocarbides, after, for example, being aged for 1000 hours at 800 °C. The nanonitride precipitates may include particles having dimensions from 5 nanometers to 100 nanometers, from 10 nanometers to 90 nanometers, or from 20 nanometers to 80 nanometers. Niobium chromium nitrides have been identified using analytical electron microscopy as rich in niobium and chromium, and as the tetragonal nitride phase by electron diffraction (both carbides are cubic phases). X-ray energy dispersive quantitative analysis has shown that for the improved alloy compositions, these nanoscale nitride particles may have a composition by weight of: 63% niobium, 28% chromium, and 6% iron, with other components being less than 1.5% each. Such niobium chromium nitrides were not observed in aged cast stainless steels with similar compositions, and appear to be a direct consequence of the wrought processing.

In some embodiments, the improved wrought alloy may include a mixture of microstructures (for example, a mixture of nanocarbides and nanonitrides). The mixture of microstructures may be responsible for the improved strength of these alloy compositions at elevated temperatures, such as, for example, 900-1000 °C. In some embodiments, the improved alloys may have a yield strength greater than 35 kpsi, or 30 kpsi at 800°C.

In some embodiments, the improved alloys are processed to produce a wrought material. Processing may include steps such as the following. A centrifugal cast pipe may be cast from the improved alloy. A section may be removed from the casting and heat treated at a temperature of at least 1250 °C for, for example, three hours. The heat treated section may be hot rolled at a temperature of at least 1200 °C to a thickness of about half

of the original thickness inches), annealed at a temperature of at least 1200 °C for fifteen minutes, and then sandblasted. The sandblasted section may be cold rolled to a thickness of about one third of the original cast thickness. The cold rolled section may be annealed to a temperature of at least 1250 °C for a period of time, for example, an hour, in, for example, air with an argon cover, and then given a final additional heat treatment for one hour at a temperature of at least 1250 °C in air with an argon blanket. An alternative process may include any of the following: initially homogenizing the cast plate at a temperature of at least 1200 °C for a period of time, for example 1-1/2 hours; hot rolling at a temperature of at least 1200 °C to two thirds of the original cast thickness; and annealing the cold-rolled plate for one hour at a temperature of at least 1200 °C. The improved alloys may be extruded at, for example, 1200 °C, with, for example, a mandrel diameter of 22.9 millimeters (0.9 inches) and a die diameter of 34.3 millimeters (1.35 inches) to produce good quality tubes.

The wrought material may be welded by, for example, laser welding or tungsten gas arc welding. Thus, tubes may be produced by rolling plates and welding seams.

Annealing the improved alloys at higher temperatures, such as 1250 °C, may improve properties of the alloys. At a higher temperature, more of the phases go into solution and upon cooling precipitate into phases that contribute positively to the properties, such as high temperature creep and tensile strength. Annealing at temperatures higher than 1250 °C, such as 1300 °C may be beneficial. For example, the calculated phase present in the improved alloys may decrease by 0.08% at 1300 °C as opposed to the phase present in the improved alloys at 1200 °C. Thus, upon cooling, more useful precipitates may form by 0.08%. Improved alloys may have high temperature creep strengths and tensile strengths that are superior to conventional alloys. For example, niobium stabilized stainless steel alloys that include manganese, nitrogen, copper and tungsten may have high temperature creep strengths and tensile strengths that are improved, or substantially improved relative to conventional alloys such as 347H.

Improved alloys may have increased strength relative to standard stainless steel alloys such as Super 304H at high temperatures (for example, 700 °C, 800 °C, or above 1000 °C). Superior high temperature creep-rupture strength (for example, creep-rupture strength at 800 °C, 900 °C, or 1250 °C) may be improved as a result of (a) composition, (b) stable, fine-grain microstructures induced by high temperature processing, and (c) age-induced precipitation structures in the improved alloys. Precipitation structures include,

for example, microcarbides that strengthen grain boundaries and stable nanocarbides that strengthen inside the grains. Presence of phases other than sigma, laves, G, and chi phases contribute to high temperature properties. Stable microstructures may be achieved by proper selection of components. High temperature aging induced or creep-induced microstructures may have minimal or no intermetallic sigma, laves and chi phases. Intermetallic sigma, laves and chi phases may weaken the strength properties of alloys and are therefore generally undesirable.

At 800 °C, the improved alloys may include at least 3% or at least 3.25% by weight of microcarbides, other phases, and/or stable, fine grain microstructure that produce strength. At 900 °C, the improved alloys may include, by weight, at least 1.5%, at least 2%, at least 3%, at least 3.5%, or at least 5% microcarbides, other phases, and/or stable, fine grain microstructure that produce strength. These values may be higher than the corresponding values in 347H or Super 304H stainless steel alloys at 900 °C. At 1250 °C improved alloys may include at least 0.5% by weight microcarbides, other phases, and/or stable, fine grain microstructure that produce strength. The resulting higher weight percent of microcarbides, other phases, and/or stable, fine grain microstructure, and the exclusion of sigma and laves phases, may account for superior high temperature performance of the improved alloys.

Alloys having similar or superior high temperature performance to the improved alloys may be derived by modeling phase behavior at elevated temperatures and selecting compositions that retain at least 1.5%, at least 2%, or at least 2.5% by weight of phases other than sigma or laves phases at, for example, 900 °C. For example, a stable microstructure may include an amount, by weight, of: niobium that is nearly ten times the amount of carbon, from 1% to 12% manganese, and from 0.15 to 0.5% of nitrogen. Copper and tungsten may be included in the composition to increase the amount of stable microstructures. The choice of elements for the improved alloys allows processing by various methods and results in a stable, fine grain size, even after heat treatments of at least 1250 °C. Many prior art alloys tend to grain coarsen significantly when annealed at such high temperatures whereas the improved alloy can be improved by such high temperature treatment. In some embodiments, grain size is controlled to achieve desirable high temperature tensile and creep properties. Stable grain structure in the improved alloys reduces grain boundary sliding, and may be a contributing factor for the better strength relative to commercially available alloys at temperatures above, for example, 650 °C.

Non-restrictive examples are set forth below.

Modeling of Alloy Phase Behavior

Modeling of phase behavior for different improved alloy compositions to determine compositions that contain increased amounts of phases that contribute positively to physical properties was performed. Compositions such as Cu, Z, M(C,N), M₂(C,N), and M₂₃C₆, may minimize the amount of phases that are embrittling phases such as G, sigma, laves, and chi. There may be other reasons to include certain components. For example, silicon is typically included in stainless steel alloys to improve processing properties, and nickel and chromium are typically included in the alloys to impart corrosion resistance. When two components may be included to accomplish the same result, then the less expensive component may be beneficially included. For example, to the extent manganese may be substituted for nickel without sacrificing performance, such a substitution may reduce the cost of the alloy at current component prices.

The effect of total phase content of the alloys similar to those described above has been found to be approximated by the equation:

$$\sigma_r = 1.0235 (\text{TPC}) + 5.5603$$

Where σ_r is the creep rupture strength for one thousand hours at 800 °C in kilo-pound per square inch (ksi) and TPC is the total phase content calculated for the composition. This estimate was further improved by only including in the TPC term the amount of Cu phase, Z phase, M(C,N) phase, M₂(C,N) phase, and M₂₃C₆ phase (the “desirable phases”), and calculating the constants on this basis. Another improvement to this estimate may be to use only the difference between the desirable phases present at the annealing temperature and at 800 °C. Thus, the components that do not go into solution in the annealing process were not considered because they do not add significantly to the strength of the alloys at elevated temperatures. For example, the difference between the amount of Cu phase, Z phase, M(C,N) phase, M₂(C,N) phase, and M₂₃C₆ phase present based on equilibrium calculations at annealing temperatures less the amount calculated to be present at 800 °C may be 1% by weight of the alloy, or it could be 1.5% by weight of the alloy or 2% by weight of the alloy, to result in an alloy with good high temperature strength. Further, the annealing temperature may be 1200 °C, or it may be 1250 °C, or it may be 1300 °C.

The improved alloys may be further understood by modeling the addition, or reduction, of different metals to determine the effect of changing amounts of that metal on the phase content of the alloy. For example, with a starting composition by weight of:

20% chromium, 3% copper, 4% manganese, 0.3% molybdenum, 0.8% niobium, 12.5% nickel, 0.5% silicon, 1% tungsten, 0.1% carbon and 0.25% elemental nitrogen, modeling with varying amounts of chromium results in included phases of $M_{23}C_6$, $M(C,N)$, $M_2(C,N)$, Z, Cu, chi, laves, G, and sigma at 800 °C, according to FIG. 2. The amount of these phases plotted in each of FIGS. 2-12 is the calculated amount of these phases at 800 °C. In FIGS. 2-12, curve 220 refers to $M_{23}C_6$, curve 222 refers to $M_2(C,N)$ phase, curve 224 refers to Z phase, curve 226 refers to Cu phase, curve 228 refers to sigma phase, curve 230 refers to chi phase, curve 232 refers to G phase, curve 234 refers to laves phase, and curve 236 refers to $M(C,N)$ phase.

FIG. 2 depicts the weight percentages of phases versus weight percentage of chromium in the alloy. As shown, the weight percentages of phases 220, 222, 224, and 226 remained relatively constant from 20% by weight to 30% by weight of chromium, while sigma phase 228 increased linearly above a chromium content of 20.5% by weight. Thus, from the modeling, a chromium content between 20% by weight and 20.5% by weight of the alloy may be favorable.

FIG. 3 depicts weight percentages of phases versus the weight percentage of silicon (Si) in the alloy. As shown in FIG. 3, varying the silicon content of the alloy resulted in sigma phase 228 appearing at levels above 1.2% by weight silicon and chi phase 230 appearing above a content of 1.4% by weight silicon. G phase 232 appeared above 1.6% by weight silicon and increased as the weight percent of silicon increased. With increasing weight percentages of silicon, phases 220, 222, and 224, remained relatively constant and a slight increase in Cu phase 226 was predicted. The appearance of sigma phase 228, chi phase 230, and G phase 232 indicates that a silicon content below 1.2% by weight in this alloy may be favorable.

FIG. 4 depicts weight percentage of phases formed versus weight percentage of tungsten in the alloy. As shown in FIG. 4, varying the weight percentage of tungsten in the alloy resulted in sigma phase 228 appearing at 1.4% by weight tungsten. Laves phase 234 appeared at 1.5% by weight tungsten and increased with increasing weight percentage of tungsten. Thus, the model predicts a tungsten content in this alloy of below 1.3% by weight may be favorable.

FIG. 5 depicts weight percentage of phases formed versus the weight percentage of niobium in the alloy. As shown in FIG. 5, modeling predicted that weight percentage of Z phase 224 increased in a linear fashion as the weight percentage of niobium increased in

the alloy until the niobium content of the alloy reached 1.55% by weight. As the niobium content increased from 0.1% by weight to 1.4% by weight, $M_2(C,N)$ phase 222 decreased fairly linearly. The decrease in $M_2(C,N)$ phase 222 was compensated for by the increase in Z phase 224, Cu phase 226 and $M_{23}C_6$ phase 220. Above 1.5% by weight niobium in the alloy, sigma phase 228 increased rapidly, Z phase 224 decreased, $M_{23}C_6$ phase 220 decreased, and $M(C,N)$ phase 236 appeared. Thus, the niobium content in the alloy of at most 1.5% by weight may maximize the weight percent of phases 220, 222, 224, and 226 and avoid minimizing the weight percent of sigma phase 228 formed in the alloy. In order to make the alloy hot-workable, it was found that at least 0.5% by weight of niobium was desirable. Thus, in some embodiments, the alloy contains from 0.5% by weight to 1.5% by weight or from 0.8% by weight to 1% by weight niobium.

FIG. 6 depicts weight percentages of phases formed versus weight percentage of carbon. As shown in FIG. 6, weight percentage of sigma phase 228 was predicted to decrease as the weight percentage of carbon in the alloy increased from 0 to 0.06. The weight percentage of $M_{23}C_6$ phase 220 was predicted to increase linearly as the weight percentage of carbon in the alloy increased to at most 0.5. $M_2(C,N)$ phase 222, Z phase 224, and Cu phase 226 was predicted to remain relatively constant as the weight percentage of carbon increased in the alloy. Since, sigma phase 228 decreased after 0.06% by weight carbon, a carbon content of 0.06% by weight to 0.2% weight in the alloy may be beneficial.

FIG. 7 depicts weight percentage of phases formed versus weight percentage of nitrogen. As shown in FIG. 7, the content of nitrogen in the alloy increased from 0% by weight to 0.15% by weight, a content of sigma phase 228 decreased from 7% by weight to 0% by weight, a content of $M(C,N)$ phase 236 decreased from 1% by weight to 0% by weight, a content of $M_{23}C_6$ phase 220 increased from 0% by weight to 1.9% by weight, and a content of Z phase 224 increased from 0% by weight to 1.4% by weight. Above a nitrogen content of 0.15% by weight in the alloy, $M_2(C,N)$ phase 222 appeared and increased with as the content of nitrogen in the alloy increases. Thus, a nitrogen content in a range of 0.15% to 0.5% by weight in the alloy may be beneficial.

FIG. 8 depicts weight percentage of phases formed versus weight percentage of titanium (Ti). As shown in FIG. 8, varying the weight percentage of titanium from 0.19 to 1 may contribute to an increase in a weight percentage of sigma phase 228 from 0 to 7.5 in the alloy. Thus, a titanium content of below 0.2% by weight in the alloy may be desirable.

As shown, as the content of titanium increased from 0% by weight to 0.2% by weight, an increase in the weight percentage of M(C,N) phase 236 occurred, a decrease in the weight percentage of $M_2(C,N)$ phase 222 occurred, and a decrease in the weight percentage Z phase 224 occurred. The decreases in the amount of $M_2(C,N)$ phase 222 and Z phase 224 appear to offset the increase in the weight percent of M(C,N) phase 236. Thus, inclusion of Ti in the alloy may be for purposes other than for increasing the amount of phases that improve properties of the alloy.

FIG. 9 depicts weight percentage of phases formed versus weight percentage of copper. As shown in FIG. 9, weight percentages of $M_{23}C_6$ phase 220, $M_2(C,N)$ phase 222, and Z phase 224 did not vary significantly as the weight percent of copper in the alloy increased. When the content of copper in the alloy increases above 2.5% by weight, Cu phase 226 increased significantly. Thus, in some embodiments, it is desirable to have more than 3% by weight copper in the alloy. In some embodiments, 10% by weight of copper in the alloy is beneficial.

FIG. 10 depicts weight percentage of phases formed versus weight percentage of manganese. As shown in FIG. 10, varying the content of manganese in the alloy did not greatly affect the weight percentage of beneficial phases $M_{23}C_6$ phase 220, $M_2(C,N)$ phase 222, Z phase 224, and Cu phase 226 in the alloy. The amount of manganese may therefore be varied in order to reduce cost, or for other reasons, without significantly effecting the high temperature properties of the alloy, with an acceptable range of manganese content of the alloy being from 2% by weight to 10% by weight.

FIG. 11 depicts weight percentage of phases formed versus weight percentage of nickel. As shown in FIG. 11, as the nickel content of the alloy increased above 8.4% by weight, a decrease in sigma phase 228 was observed. As the Ni content of the alloy was increased from 8% by weight to 17% by weight, Cu phase 226 decreased almost linearly until it disappeared at 17% by weight and a small increase in the weight percentage of $M_2(C,N)$ phase 222 was predicted. From the model, a content of nickel of 10% by weight to 15% by weight in the alloy, or in other embodiments, a nickel content of 12% by weight to 13% by weight in the alloy may avoid the formation of sigma phase 228, while improvements in corrosion properties offset any detrimental effect of less Cu phase 226.

FIG. 12 depicts weight percentage of phases formed versus weight percentage of molybdenum. As shown in FIG. 12, the weight percentage of beneficial phases $M_{23}C_6$ phase 220, $M_2(C,N)$ phase 222, Z phase 224, and Cu phase 226 remained relatively

constant as the weight percentage of molybdenum in the alloy was varied. As Mo content of the alloy exceeded 0.65% by weight, the weight percentages of sigma phase 228 and chi phase 230 in the alloy increased significantly with no significant changes in the other phases. The content of molybdenum in the alloy, in some embodiments, may therefore be limited to at most 0.5% by weight.

Alloy Examples

Alloys A through N were prepared according to TABLE 1. Measured compositions are included in the TABLE 1 when such measurements are available. The total phase content of the alloys is calculated for the listed composition.

TABLE 1

Alloy		% by weight											
		Cr	Cu	Mn	Mo	Nb	Ni	Si	W	C	N	Ti	800° C Total Phase
A	Target	20	--	4	0.3	0.8	12.5	0.5	--	0.09	0.25	--	
	Actual ^b	19	--	4.2	0.3	0.8	12.5	0.5	--	0.09	0.24	--	3.35 ^a
B	Target	20	3	4	0.3	0.8	13	0.5	1	0.09	0.25	--	
	Actual-1 ^b	20	3	4	0.3	0.77	13	0.5	1	0.09	0.26	--	4.40 ^a
	Actual-2 ^b	20.35	2.94	4.09	0.28	0.76	12.52	0.44	1.03	0.09	0.23	--	
	Actual-3 ^{b,c}	18.78	2.94	2.85	0.29	0.65	12.75	0.39	1.03	0.10	0.23	0.004	
C	Target	20	4.5	4	0.3	0.8	12.5	0.5	1	0.15	0.25	--	7.15
	Actual-1 ^b	18.74	4.37	3.68	0.29	0.77	13.00	0.43	1.18	0.11	0.17	0.002	5.45
	Actual-2 ^{c,b}	20.48	4.75	4.13	0.30	0.07	12.81	0.52	1.18	0.17	0.14	0.01	6.23
D	Target	20	4.5	4	0.3	0	12.5	0.5	1	0.2	0.5	0	10
E	Target	20	4	4	0.5	0.8	12.5	0.5	1	0.1	0.3	--	6.2
	Actual	18.84	4.34	3.65	0.29	0.75	12.93	0.43	1.21	0.09	0.2	0.002	5.3
F	Target	20	3	1	0.3	0.77	13	0.5	1	0.09	0.26	--	4.7
	Actual ^b	18.97	2.88	0.92	0.29	0.74	13.25	0.43	1.17	0.05	0.12	<0.001	2.45
G	Target	20	4.5	4	0.3	0.8	7	0.5	1	0.2	0.5	--	
	Actual ^e	20.08	4.36	4	0.3	0.81	7.01	0.5	1.04	0.24	0.31	0.008	9.6 ^a
H	Target	21	3	3	0.3	0.80	7	1	2	0.1	0.4	--	
	Actual ^e	21.1	2.95	3.01	0.31	0.82	6.98	0.51	2.06	0.13	0.32	<0.001	13.46 ^f
I	Target	21	3	8	0.3	0.80	7	0.5	1	0.1	0.5	--	7.1
	Actual ^e	21.31	2.94	7.95	0.31	0.83	7.02	0.52	1.05	0.13	0.37	0.003	9.45
J	Target	20	4	2	0.5	1.00	12.5	1	1	0.20	0.50	--	9.8
	Actual ^e	19.93	3.85	2.13	0.5	0.99	12.11	1.08	1.01	0.23	0.29	0.022	8.95
K	Target	20	3	4	0.3	0.77	13	0.5	1	0.09	0.26	--	
	Actual ^e	18.94	2.96	4.01	0.31	0.81	13.05	0.52	1.03	0.12	0.35	0.018	5.62
L	Target	20	3	4	0.3	0.10	13	0.5	1	0.09	0.26	--	
	Actual ^b	20.06	2.96	3.95	0.3	0.12	12.93	0.59	1.03	0.11	0.25	0.005	4.28
M	Target	20	3	4	0.3	0.50	13	0.5	1	0.09	0.26	--	
	Actual ^b	20.11	2.93	3.98	0.3	0.51	12.94	0.5	1.03	0.12	0.13	<0.001	2.76
N	Target	20	3.4	4	1	0.80	12.5	0.5	2	0.1	0.3		8.85 ^g

^aCalculated using actual composition; ^bNonconsumable-arc melted; ^cRemelted by element compensation; ^dContains 1.7% sigma phase and 1.55% laves phase; ^eInduction melted; ^f

Contains 3.9% sigma phase and 1.7% chi phase; [§]Includes 1.7% sigma and 1.55% laves phases.

Hot working with Niobium Example

To determine the capability for alloys to be hot worked, samples of alloys C, D, E, F, K, L, and M in TABLE 1 were prepared by arc-melting one pound samples into ingots of 25.4 millimeter x 25.4 millimeter x 101.6 millimeter (1 inch x 1 inch x 4 inch). After cutting hot-tops and removing some shrinkage underneath, each sample was homogenized at 1200 °C for one hour, and then hot-rolled to a thickness of 12.7 millimeter (0.5 inch) at 1200 °C with intermediate heat. The samples were then cold rolled to a 6.34 millimeter (0.25 inch) thick plate and vacuum annealed at 1200 °C for one hour.

When alloy D (0% by weight niobium) was hot rolled, it cracked and the rolling to 12.7 millimeter (0.5 inch) thickness could not be accomplished. Alloy L (0.12% by weight niobium) could be hot-rolled, but developed cracks from the edge of the samples progressing toward the center of the sample, and would not be a useful material after such hot rolling. Alloy M (0.51% Nb) could be hot-rolled, without developing cracks or any other problems. The other samples were processed using the above described procedure without any problems, resulting in 6.35 millimeter (0.25 inch) plates that were free of cracks. It has been found that even 0.07% by weight niobium in the alloy composition may significantly reduce the tendency of the alloy to develop cracks during hot working. An alloy having at least 0.5% by weight niobium can be incorporated in wrought alloys to improve properties such as hot workability. Some alloys may have by weight from 0.5% to 1.2% niobium, from 0.6% to 1.0% niobium, or from 0.7% to 0.9% niobium to improve the alloy properties.

High Temperature Heat Treating Example

Samples of alloys A and B from TABLE 1 were processed by two different methods. Process A included a heat treating and an annealing step at a temperature of 1200 °C. Process B included a heat treating and an annealing step at a temperature of 1250 °C. With the higher heat treating and annealing temperatures, measurable improvements in yield strength and ultimate tensile strength were observed for the two alloys when processed at the higher temperature.

The process at a temperature of 1200 °C was accomplished as follows: sections of 15.24 cm (six inch) ID by 3.81 cm (1.5 inches) thick centrifugally cast pipe were homogenized at a temperature of 1200 °C for one and a half hours; a section was then hot-

rolled at 1200 °C to a 25.4 cm (one inch) thickness for alloy A and a 1.91 cm (three-quarter inch) thickness for alloy B; after cooling to room temperature, the plates were annealed at 1200 °C for fifteen minutes; the plates were then cold-rolled to a thickness of 13.97 millimeter (0.55 inches). The cold-rolled plates were annealed for one hour at 1200 °C in air under an argon blanket. The annealed plates were annealed for a final time at 1250 °C for one hour in air under an argon blanket. This process is referred to herein as process A.

The process with higher heat treating and annealing temperatures varied from the above procedure by homogenization of the cast plates at a temperature of 1250 °C for three hours instead of one and a half hours; hot rolling was carried out at 1200 °C from a 38.1 millimeter (1.5 inch) thickness to a 19.05 millimeter (0.75 inch) thickness; and the resulting plate was annealed for fifteen minute at 1200 °C followed by cold-rolling to 13.97 millimeter (0.55 inch) thickness. This process is referred to herein as process B.

FIGS. 13-17 depict yield strengths and ultimate tensile strengths for different metals. In Fig. 13, data 238 shows yield strength and data 240 shows ultimate tensile strength for alloy A treated by process A. Data 242 shows yield strength and data 244 shows ultimate tensile strength for alloy B treated by process B. Data 246 shows yield strength and data 248 shows ultimate tensile strength for 347H stainless steel.

In FIG. 14, data 250 show yield strength of alloy G treated by process A. Data 252 and 254 show yield strength for alloys H and I. Data 256 shows yield strength of alloy B treated by process A. Data 258 shows yield strength of alloy B treated by process B. Data 246 shows yield strength for 347H stainless steel.

In FIG. 15, data 260 show ultimate tensile strength of alloy G treated by process A. Data 262 and 264 show ultimate tensile strength for alloys H and I. 266 shows ultimate tensile strength of alloy B treated by process A. Data 268 shows ultimate tensile strength of alloy B treated by process B. Data 248 shows ultimate tensile strength for 347H stainless steel.

In FIG. 16, data 270 and 272 show yield strength for alloys J and K. Data 256 shows yield strength of alloy B treated by process A. Data 258 shows yield strength of alloy B treated by process B. Data 246 shows yield strength for 347H stainless steel.

In FIG. 17 data 274 and 276 show ultimate tensile strength for alloys J and K. Data 266 shows ultimate tensile strength of alloy B treated by process A. Data 268 shows ultimate tensile strength of alloy B treated by process B. Data 248 shows ultimate tensile strength for 347H stainless steel.

Both ultimate tensile strength and yield strength were greater for the alloys treated at higher temperatures as compared to 347H stainless steel. A considerable improvement over 347H can be seen for alloys A, B, G, H, I, J, and K. For example, alloys A, B, G, H, I, J, and K retained tensile properties to test temperatures of 1000 °C. For an application where yield strength of 20 ksi was needed, alloys A, B, G, H, I, J, and K provide the needed yield strength for at least an additional 250 °C. For a 5 ksi difference between yield and ultimate tensile strength at test temperatures, alloys A, B, G, H, I, J, and K may be used at temperatures of 950 °C and 1000 °C as opposed to only 870 °C for 347H.

Samples of Alloy B, treated by process A and by process B were subjected to stress-rupture tests and the results are tabulated in TABLE 2. It can be seen from Table 2 that process B, with a higher annealing temperature, resulted in 47% to 474% improvement in time to rupture.

TABLE 2

Temperature (°C)	Stress (MPa)	Process A life (hours)	Process B life (hours)	Improvement by Process B
800	100	164.2	241.6	47%
850	70	32	151.7	474%
850	55	264.1	500.7	90%
900	42	90.1	140.1	55%

High Temperature Yield After Cold Work and Aging Example

A sample of alloy B, processed by process B, was aged at 750 °C for 1000 hours after being cold worked by 2.5%, 5%, and 10%, and without cold working. After aging, each was tested for tensile strength and yield strength at 750 °C. Results are tabulated in TABLE 3. It can be seen from TABLE 3 that the yield strength increased significantly as a result of cold work and high temperature aging. The ultimate tensile strength at 750 °C decreased only slightly as a result of the high temperature aging and cold working. The annealed only sample and the aged only sample were also tested at room temperature for yield strength and ultimate tensile strength. The yield strength at room temperature increased from 307 MPa to 318 MPa as a result of the aging. The ultimate tensile strength decreased from 720 MPa to 710 MPa as a result of the high temperature aging.

TABLE 3

	Annealed	Aged	2.5% Cold Worked and aged	5% Cold Worked and aged	10% Cold Worked and aged
Yield Strength, MPa	170	212	235	290	325
Ultimate Tensile Strength, MPa	372	358	350	360	358

These characteristics may be compared to competing alloys, such as 347H, which significantly lose high temperature properties as a result of only, for example, 10% cold work. Because fabrication of tubulars and heaters useful in an in situ heat treatment process often require cold work for their fabrication, improvement of some high temperature properties, or at least lack of significant loss of high temperature properties may be a significant advantage for alloys having these characteristics. It may be particularly advantageous when these properties are improved, or at least not significantly decreased, by high temperature aging.

Creep Example

Samples of alloys were subjected to 100 MPa stress at 800 °C in a nitrogen with 0.1% oxygen test environment. Each of the samples was first annealed for one hour at 1200 °C. TABLE 4 shows the time to rupture, elongation at rupture, and total phase content, where the total phase content is known.

TABLE 4

Alloy	Rupture time (hr)	Elongation (%)	Total Phase Content % at 800 °C	Comments
B	283	7.6	4.4	
B	116	5.6	4.4	
B	127	3.9	4.4	10% cold work
B	228	3.1	4.4	10% cold work
B	185	2.3	4.4	Laser weld

Alloy	Rupture time (hr)	Elongation (%)	Total Phase Content % at 800 °C	Comments
C	60	5.3	5.45	
C	137	3.6	5.45	Repeated test
E	165	5.1	5.3	
F	24	6.6	2.45	
G	178	11.3	9.6	
H	183	9.8	13.46 total 7.86 good phases	
I	228	12.6	9.45	
J	240	19.7	8.95	
K	123	14.2	5.62	
N	147	7.4	8.85	
347H	1.87	92	0.75	As received
347H	2.1	61	0.75	As received
NF709	56	32		Annealed
NF709	30	29.4		
NF709	36	26		Cold Strain 10%
NF709	82	30.6		Cold Strain 10%
NF709	700	16.2		Cold Strain 15%
NF709	643	11.4		Cold Strain 20%
NF709	1084	6		Cold Strain 20%
NF709	754	37.6		As received

A sample of the improved alloy B was rolled processed and rolled into a tube, and the seam welded, to form a 31.75 millimeter (1.25 inch) OD pipe. The pipe was then cut

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and welded back together in order to test the strength of the weld. The filler metal was ERNiCrMo-3, and the weld was completed with argon shielding gas and three passes with a preheat minimum temperature of 50 °C and an interpass maximum temperature of 350 °C. Creep failure was tested for the segment of welded pipe at 44.8 MPa and 900 °C. A rupture time of 41 hours was measured with failure at a strain of 5.5%. This demonstrated that the weld, including the heat affected zone around the weld, was not significantly weaker than the base alloy.

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 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.

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CLAIMS:

1. A heater system comprising:
a heat generating element; and
a canister surrounding the heat generating element, wherein the canister is at
5 least partially made of a material comprising:
from 18 percent to 22 percent by weight chromium;
from 5 percent to 14 percent by weight nickel;
from 1 percent to 10 percent by weight copper;
from 0.5 percent to 1.5 percent by weight niobium;
10 from 36 percent to 70.5 percent by weight iron;
from 1 percent to 10 percent by weight manganese;
from 0.12 percent to about 0.5 percent by weight nitrogen; and
from about 0.08 percent to about 0.2 percent by weight carbon;
wherein the composition, when at 800 °C, has at least two percent by weight of
15 precipitates comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N) or
M₂₃C₆ phases, where M is nickel, copper, niobium, iron or manganese, wherein the
precipitates comprise nanonitrides, the nanonitrides comprising particles having dimensions in
the range of five to one hundred nanometers.
2. The heater system as claimed in claim 1, wherein the heat generating element
20 is an electrical powered heat generating element.
3. The heater system as claimed in claim 1 or 2, wherein the heat generating
element is a hydrocarbon fuel burning element.

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4. A system for heating a subterranean formation comprising a tubular, the tubular at least partially made from a material comprising:

from 18 percent to 22 percent by weight chromium;

from 10 percent to 14 percent by weight nickel;

5 from 1 percent to 10 percent by weight copper;

from 0.5 percent to 1.5 percent by weight niobium;

from 36 percent to 70.5 percent by weight iron;

from 1 percent to 10 percent by weight manganese;

from 0.12 percent to about 0.5 percent by weight nitrogen; and

10 from about 0.08 percent to about 0.2 percent by weight carbon;

wherein the composition, when at 800 °C, has at least two percent by weight of precipitates comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N) or M₂₃C₆ phases, where M is nickel, copper, niobium, iron or manganese, wherein the precipitates comprise nanonitrides, the nanonitrides comprising particles having dimensions in
15 the range of five to one hundred nanometers.

5. The system as claimed in claim 4, wherein a heating medium is circulated through the tubular to heat the subterranean formation.

6. The system as claimed in claim 4 or 5, wherein the heating medium comprises steam.

20 7. The system as claimed in any one of claims 4-6, wherein the heating medium comprises carbon dioxide.

8. The system as claimed in any one of claims 4-7, wherein the heating medium is heated at the surface by exchanging heat with helium.

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9. The system as claimed in claim 8, wherein the helium is heated in a nuclear reactor.
10. The system as claimed in any one of claims 4-9, wherein the system further comprises an electrically powered heating element as a source of heat.
- 5 11. The system as claimed in any one of claims 4-10, wherein the tubular is fabricated by welding a rolled plate of material to form a tubular.
12. The system of as claimed in claim 11, wherein the welding comprises laser welding.
13. The system of as claimed in claim 11, wherein the welding comprises gas
10 tungsten arc-welding.
14. The heater system of claim 1, wherein the material comprises from about 3.5 percent to about 5 percent by weight manganese.
15. The heater system of claim 1, wherein the material comprises from about 0.2 percent to about 0.5 percent by weight nitrogen.
- 15 16. The heater system of claim 1, wherein the material further comprises from about 0.08 percent to about 0.2 percent by weight carbon.
17. The heater system of claim 1, wherein the material comprises carbon and at least one of the nanonitrides comprises carbon nitride.
18. The heater system of claim 1, wherein the nanonitrides comprise particles
20 having dimensions in a range of 5 nanometers to 100 nanometers.
19. The heater system of claim 1, wherein the nanonitride precipitates comprise niobium.
20. The heater system of claim 1, wherein the nanonitride precipitates comprise chromium.

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21. The heater system of claim 1, wherein the nanonitride precipitates comprise iron.
22. The heater system of claim 1, wherein the material has a yield strength of greater than 35 ksi at 800° C.
- 5 23. The heating system of claim 4, wherein the material is fabricated by heating to an annealing temperature, and wherein the material comprises at least 1.5 percent by weight more Cu, M(C,N), M₂(C,N) or M₂₃C₆ phases selected from a group consisting of Cu, M(C,N), M₂(C,N) or and M₂₃C₆ phases at 800°C than the material comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N) and M₂₃C₆ phases at the annealing temperature,
10 where M is nickel, copper, niobium, iron, or manganese.
24. The heating system of claim 23, wherein the annealing temperature is at least 1250 °C.
25. The heating system of claim 23, wherein the annealing temperature is between 1300 °C and below the melting temperature of the composition.
- 15 26. The heating system of claim 4, wherein the material comprises from about 0.2 percent to about 0.5 percent by weight nitrogen.
27. The heating system of claim 4, wherein the material comprises from about 3 percent to about 5 percent by weight manganese.
28. A method of heating a subterranean formation comprising:
20 positioning one or more heater systems in a subterranean formation, wherein at least one of the heater systems comprises:
a heat generating element; and
a canister surrounding the heat generating element, wherein the canister is at least partially made of a material comprising:

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from about 18 percent to about 22 percent by weight chromium;

from about 5 percent to about 14 percent by weight nickel;

from about 1 percent to about 10 percent by weight copper;

from above 0.5 percent to about 1.5 percent by weight niobium;

5 from about 36 percent to about 70.5 percent by weight iron;

from 1 percent to 10 percent by weight manganese;

from 0.12 percent to about 0.5 percent by weight nitrogen;

from about 0.08 percent to about 0.2 percent by weight carbon;

10 wherein the composition, when at 800 °C, has at least two percent by weight of precipitates comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N) or M₂₃C₆ phases, where M is nickel, copper, niobium, iron or manganese, wherein the precipitates comprise nanonitrides, the nanonitrides comprising particles having dimensions in the range of five to one hundred nanometers; and

15 allowing heat from the heater system to heat at least a portion of the subterranean formation.

29. The method of claim 28, wherein the heat generating element is an electrical powered heat generating element.

30. The method of claim 28, wherein the material comprises from about 0.2 percent to about 0.5 percent by weight nitrogen.

20 31. The method of claim 28, wherein the material is fabricated by heating to an annealing temperature, and the material comprises at least 1.5 percent by weight more phases selected from a group consisting of Cu, M(C,N), M₂(C,N) and M₂₃C₆ phases at 800 °C than the material comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N)

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and $M_{23}C_6$ phases at the annealing temperature, where M is nickel, copper, niobium, iron, or manganese.

32. The method of claim 31, wherein the annealing temperature is at least 1250 °C.

33. The method of claim 31, wherein the annealing temperature is between
5 1300 °C and below the melting temperature of the material.

34. The method of claim 28, wherein the material comprises from about 0.2 percent to about 0.5 percent by weight nitrogen, and wherein a weight percent ratio of manganese to nitrogen ranges from 20 to 25.

35. The method of claim 28, wherein the material comprises from about
10 3.5 percent to about 5 percent by weight manganese.

36. The method of claim 28, wherein the material further comprises nanonitrides.

37. The method of claim 28, wherein the material further comprises nanocarbides and nanonitrides, and the nanonitrides comprise carbon.

38. The method of claim 28, wherein the material further comprises nanocarbide
15 precipitates.

39. The method of claim 28, wherein the material is fabricated by heating the material to a temperature of at least 800 °C, and wherein the material at 800 °C has at least 3.25 percent by weight of precipitates.

40. The method of claim 28, wherein the material has a yield strength of greater
20 than 35 ksi at 800 °C.

41. A method of heating a subterranean formation, comprising:

positioning one or more heater systems in a subterranean formation, wherein at least one of the heater systems comprises a tubular and at least a portion of the tubular is made from a material comprising:

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from about 18 percent to about 22 percent by weight chromium;

from about 5 percent to about 14 percent by weight nickel;

from about 1 percent to about 10 percent by weight copper;

from above 0.5 percent to about 1.5 percent by weight niobium;

5 from about 36 percent to about 70.5 percent by weight iron;

from 1 percent to 10 percent by weight manganese;

from 0.12 percent to about 0.5 percent by weight nitrogen;

from about 0.08 percent to about 0.2 percent by weight carbon;

10 wherein the composition, when at 800 °C, has at least two percent by weight of precipitates comprising phases selected from the group consisting of Cu, M(C,N), M₂(C,N) or M₂₃C₆ phases, where M is nickel, copper, niobium, iron or manganese, wherein the precipitates comprise nanonitrides, the nanonitrides comprising particles having dimensions in the range of five to one hundred nanometers; and

15 allowing heat from the heater system to heat at least a portion of the subterranean formation.

42. The method of claim 41, wherein the tubular is fabricated by welding a rolled plate of material to form the tubular.

43. The method of claim 42, wherein the welding comprises laser welding.

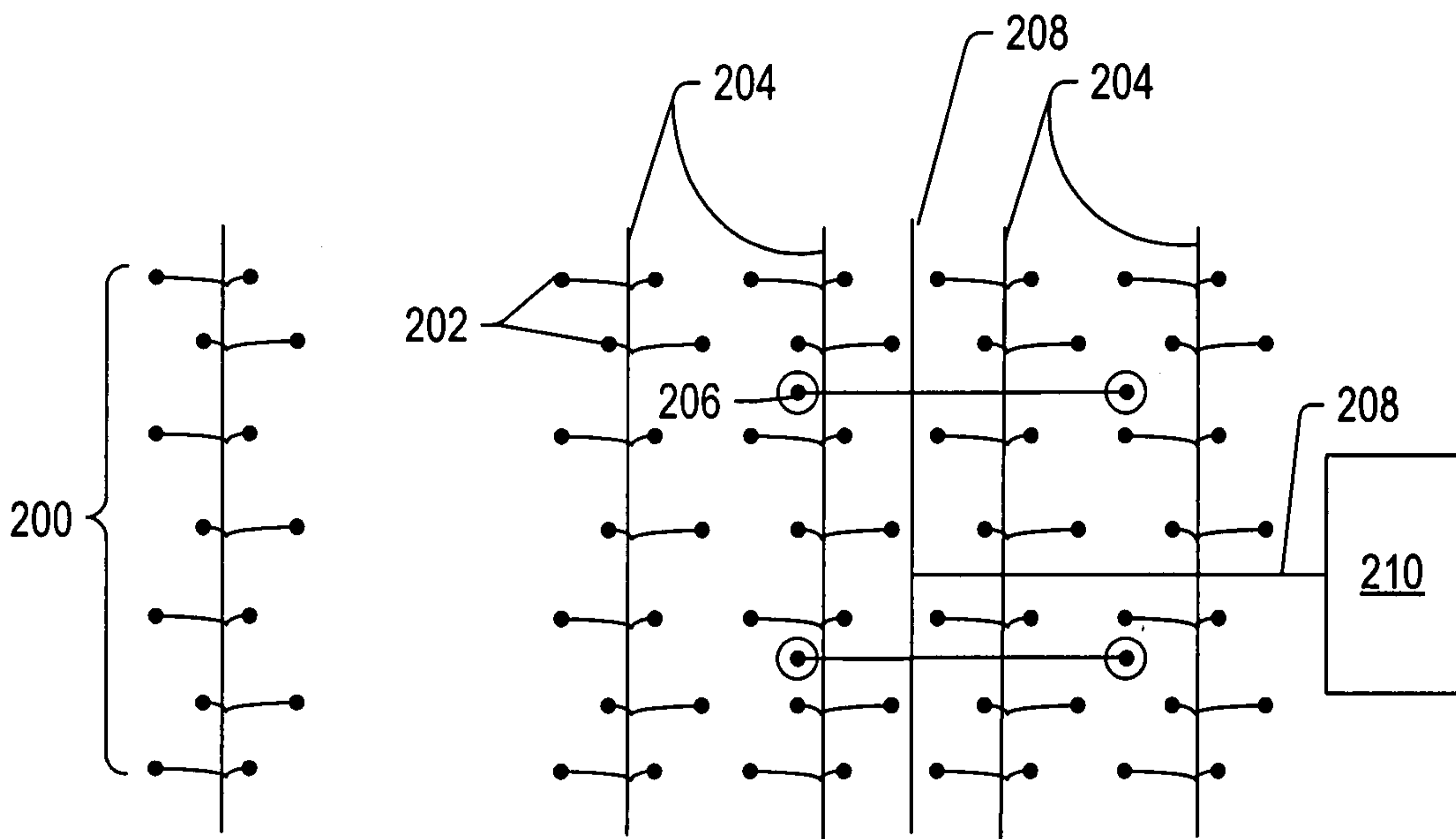


FIG. 1

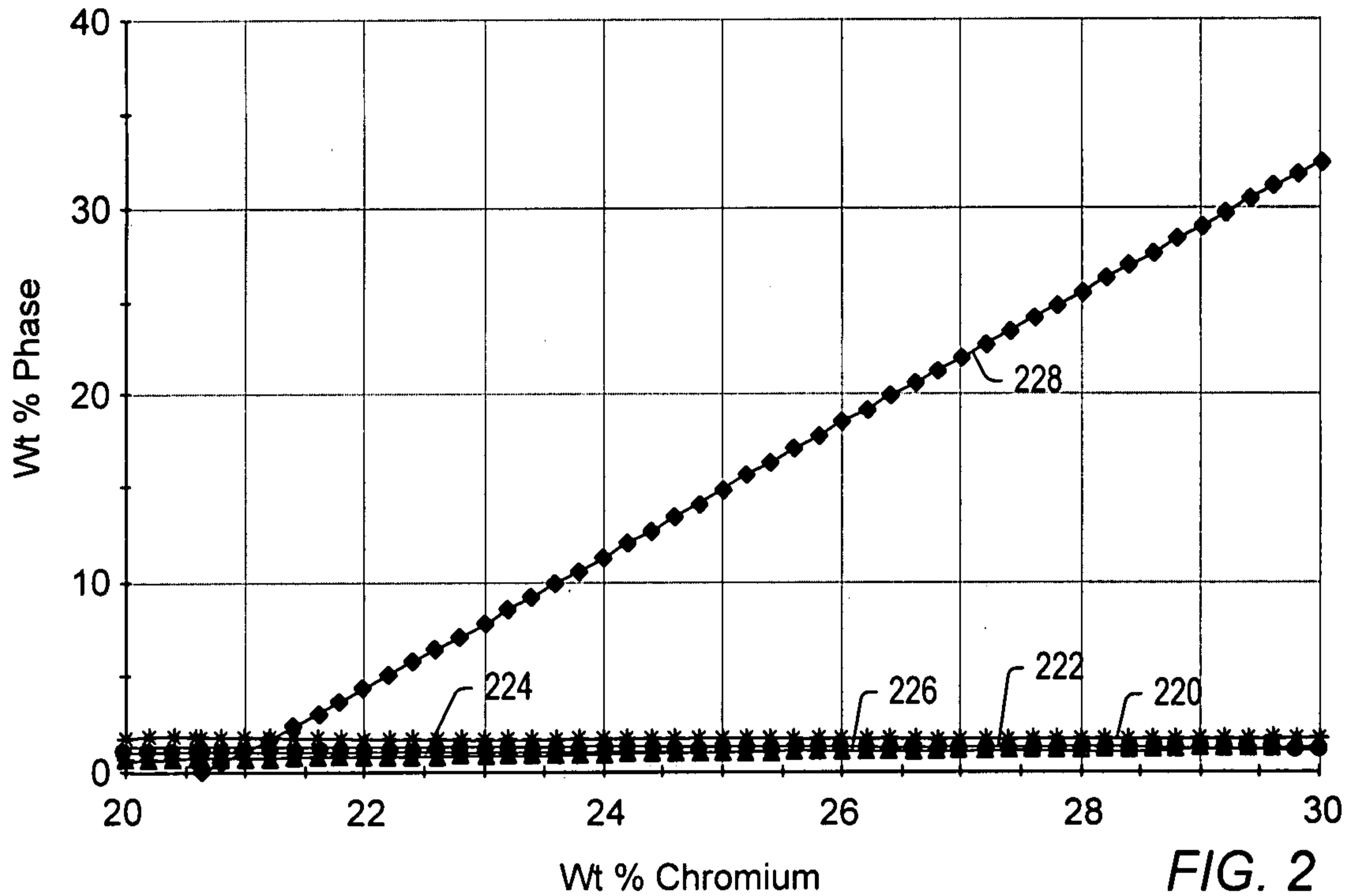


FIG. 2

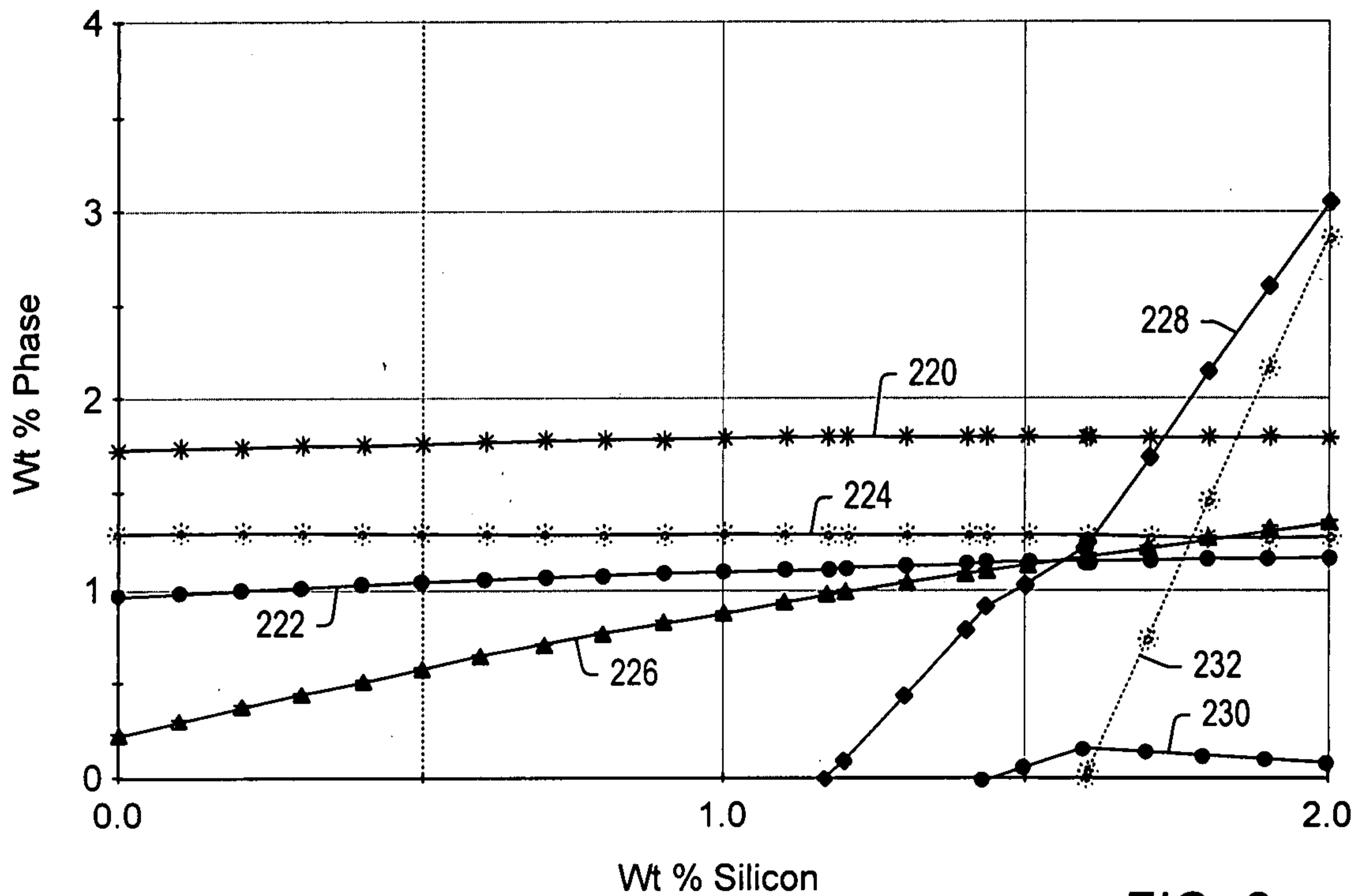


FIG. 3

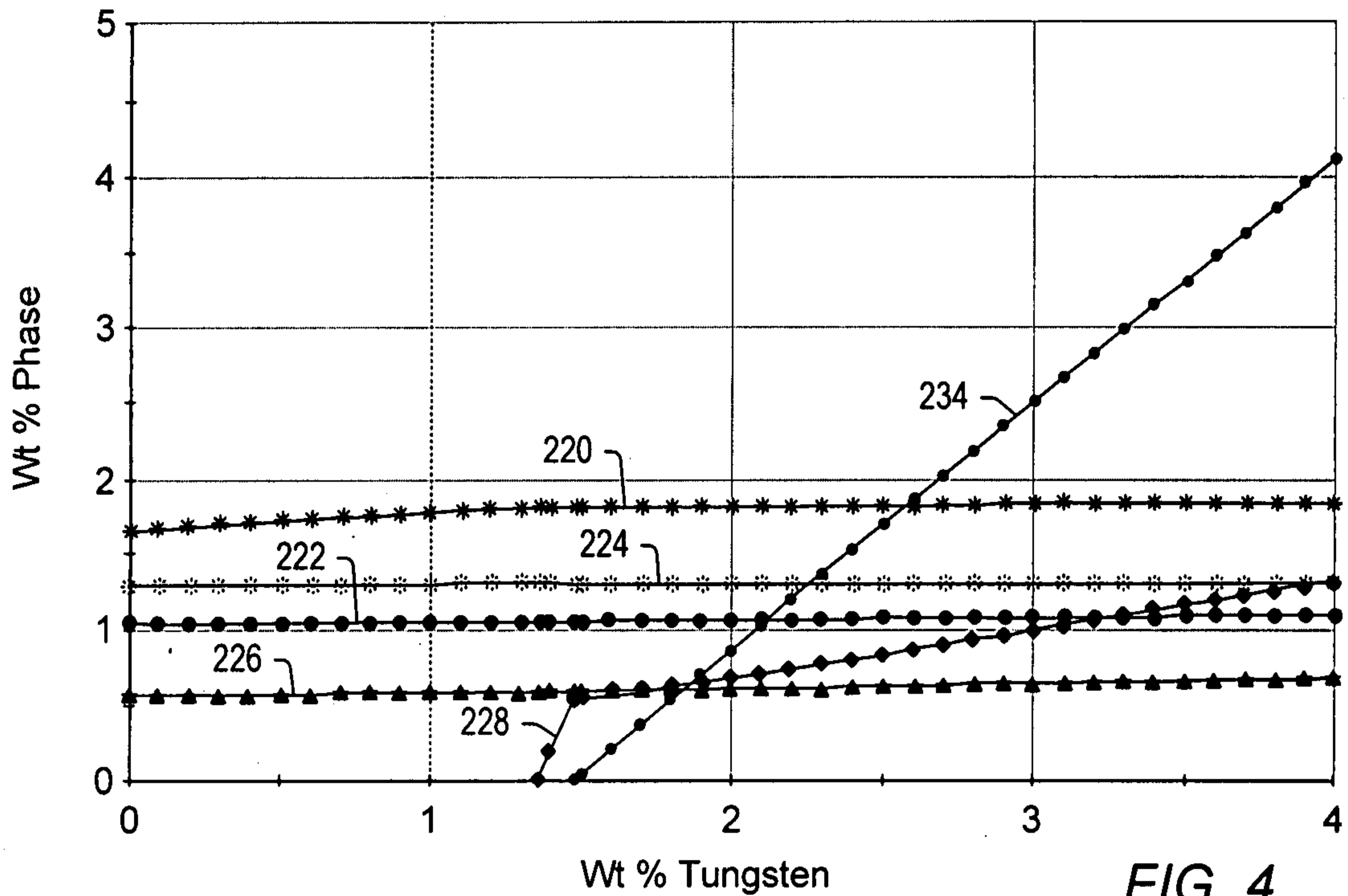


FIG. 4

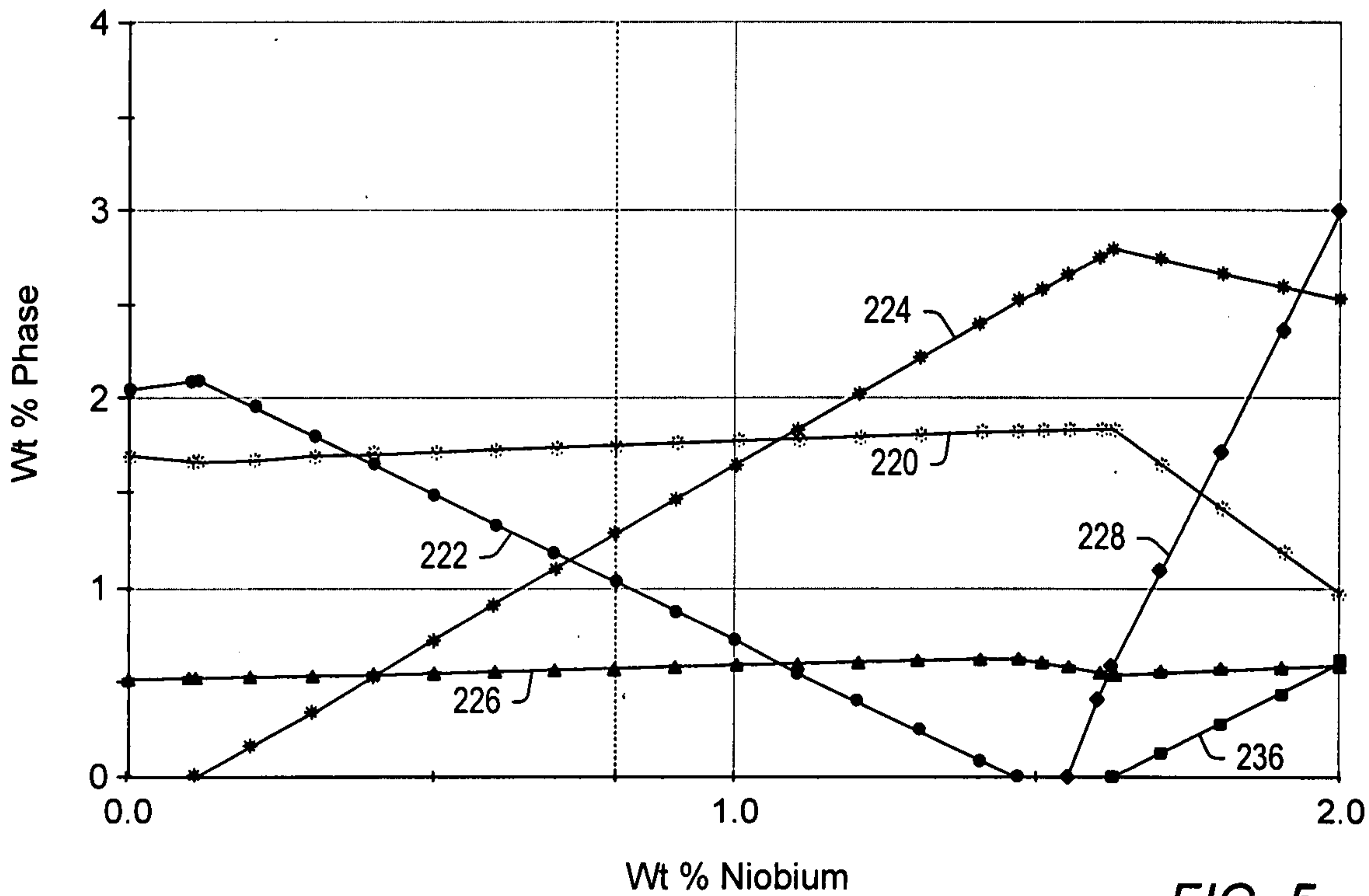


FIG. 5

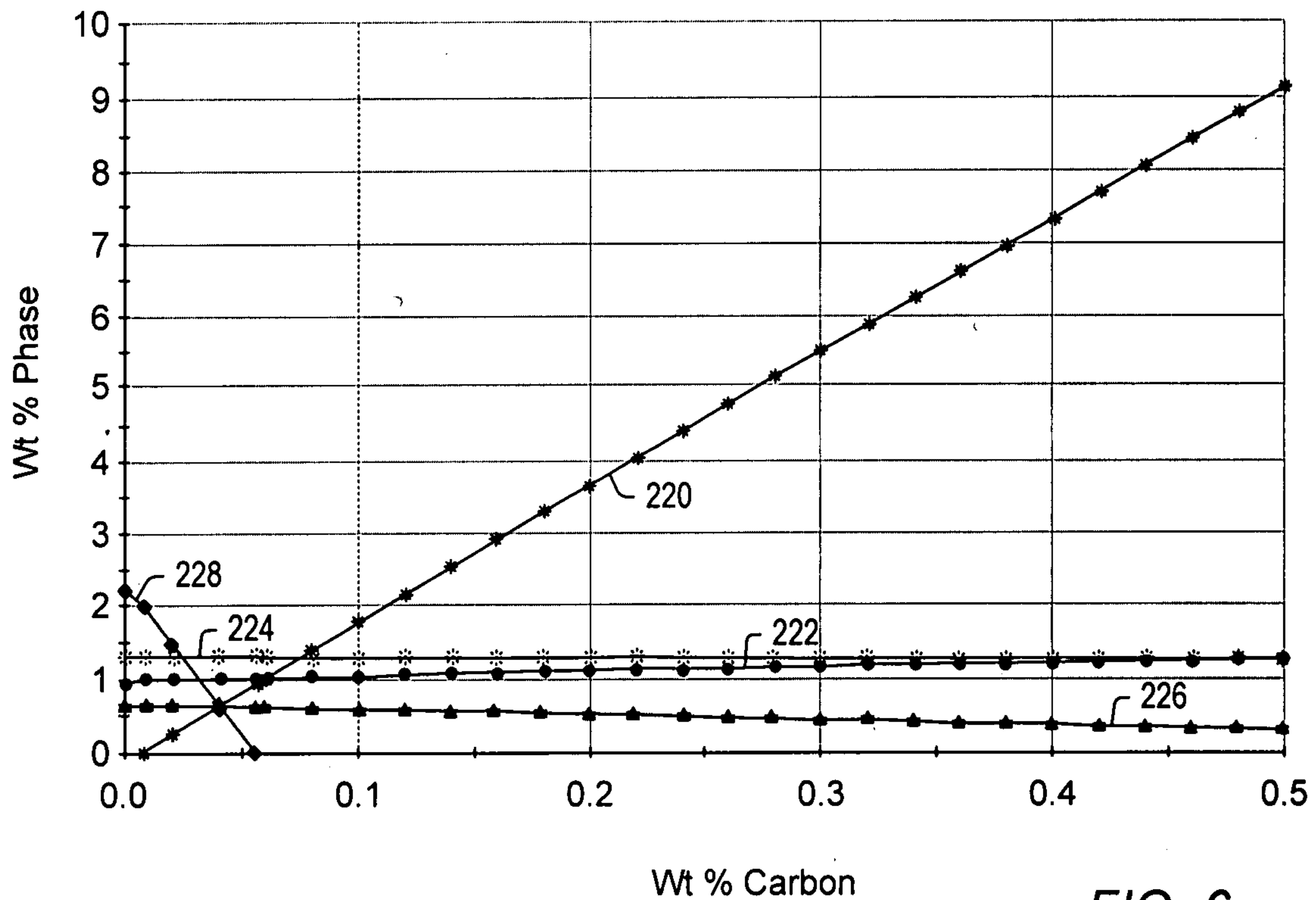


FIG. 6

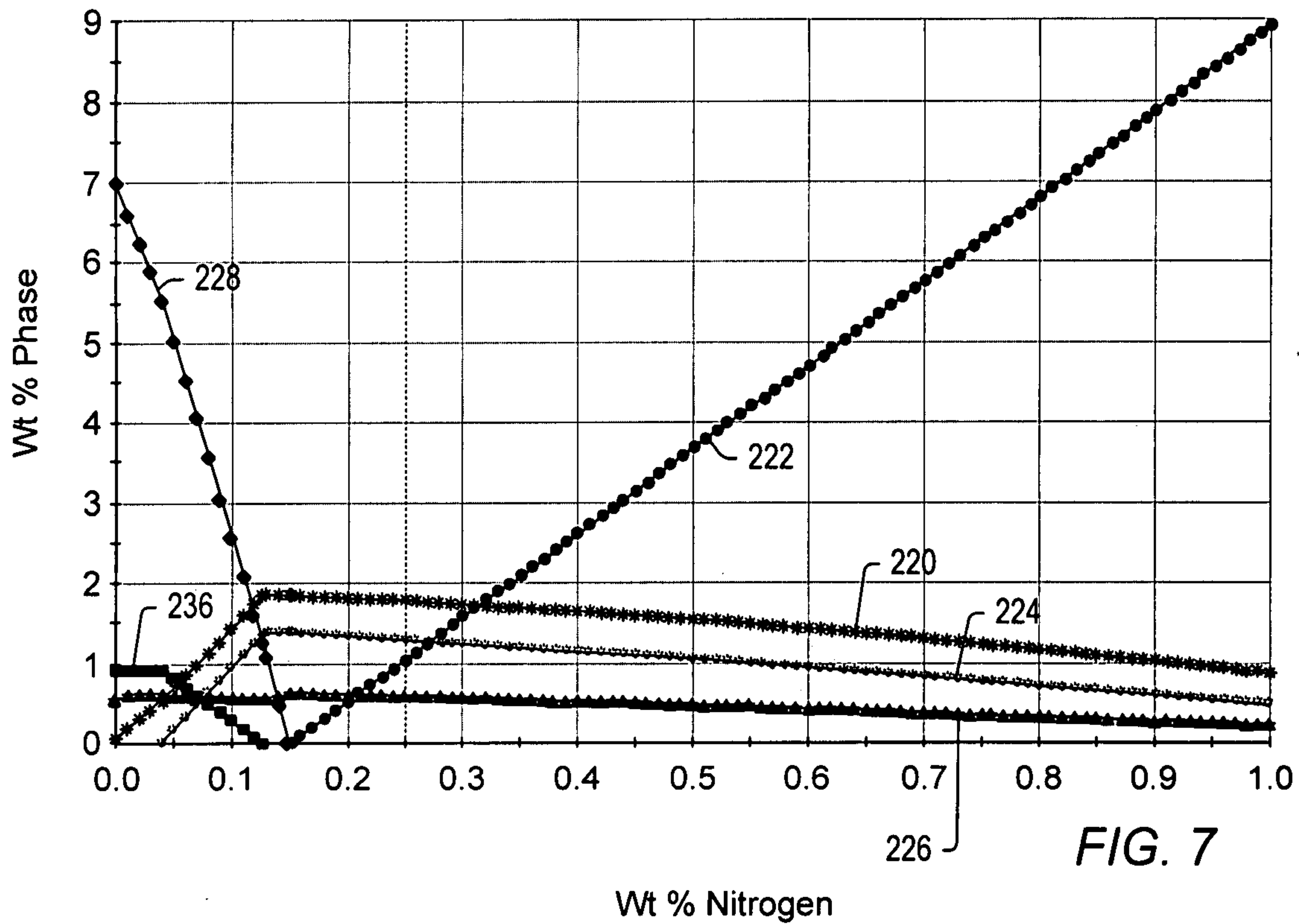


FIG. 7

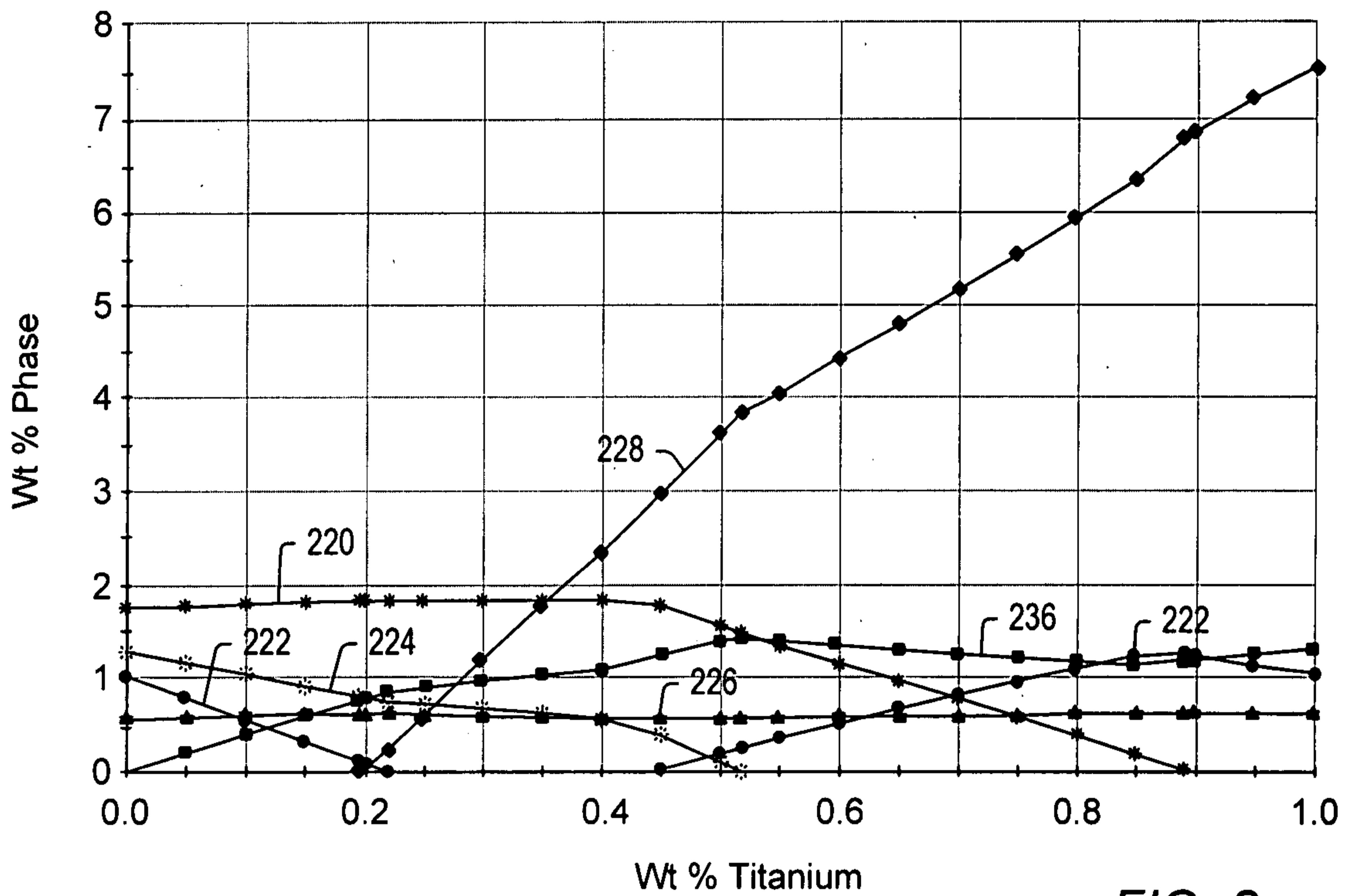


FIG. 8

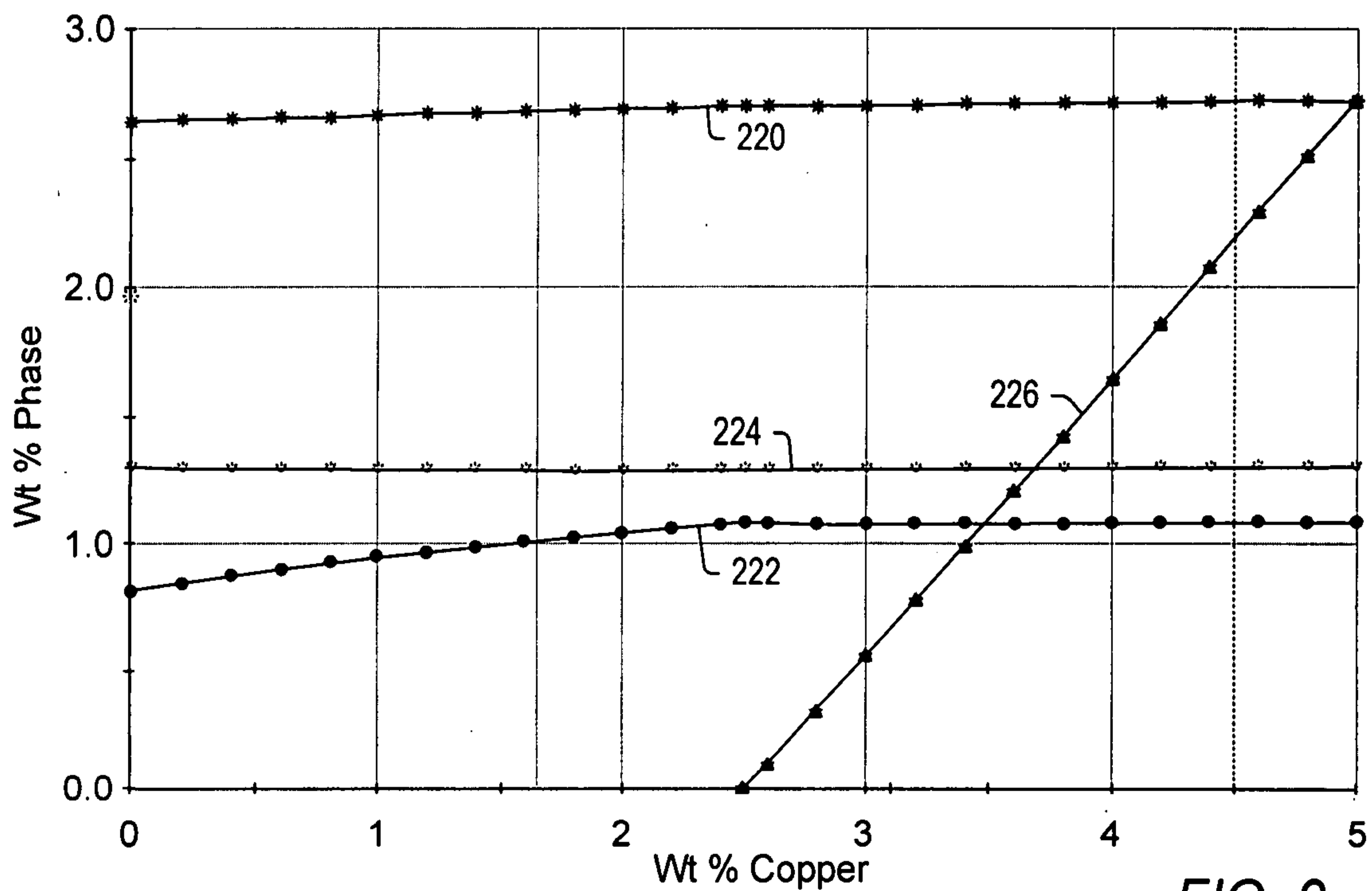


FIG. 9

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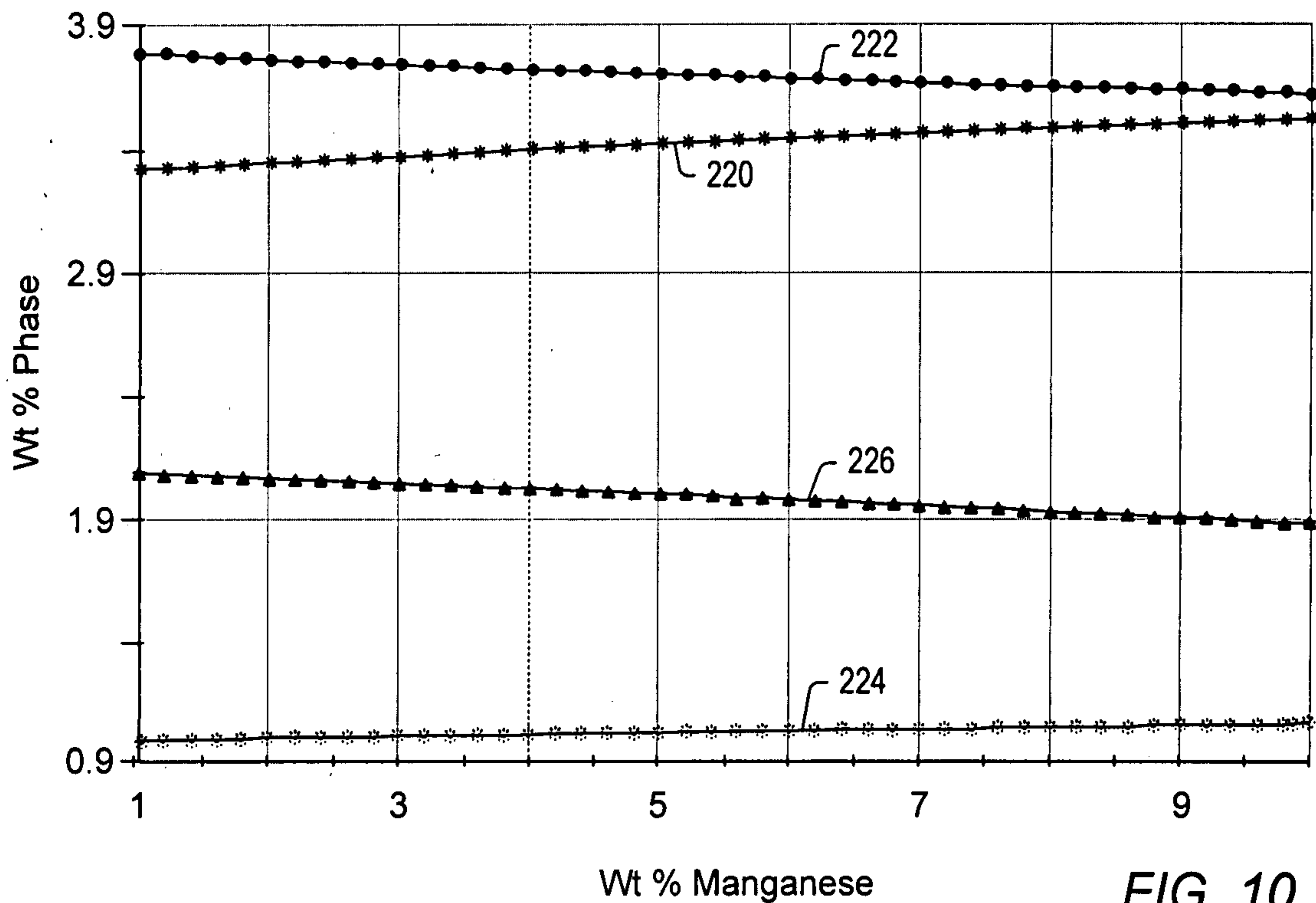


FIG. 10

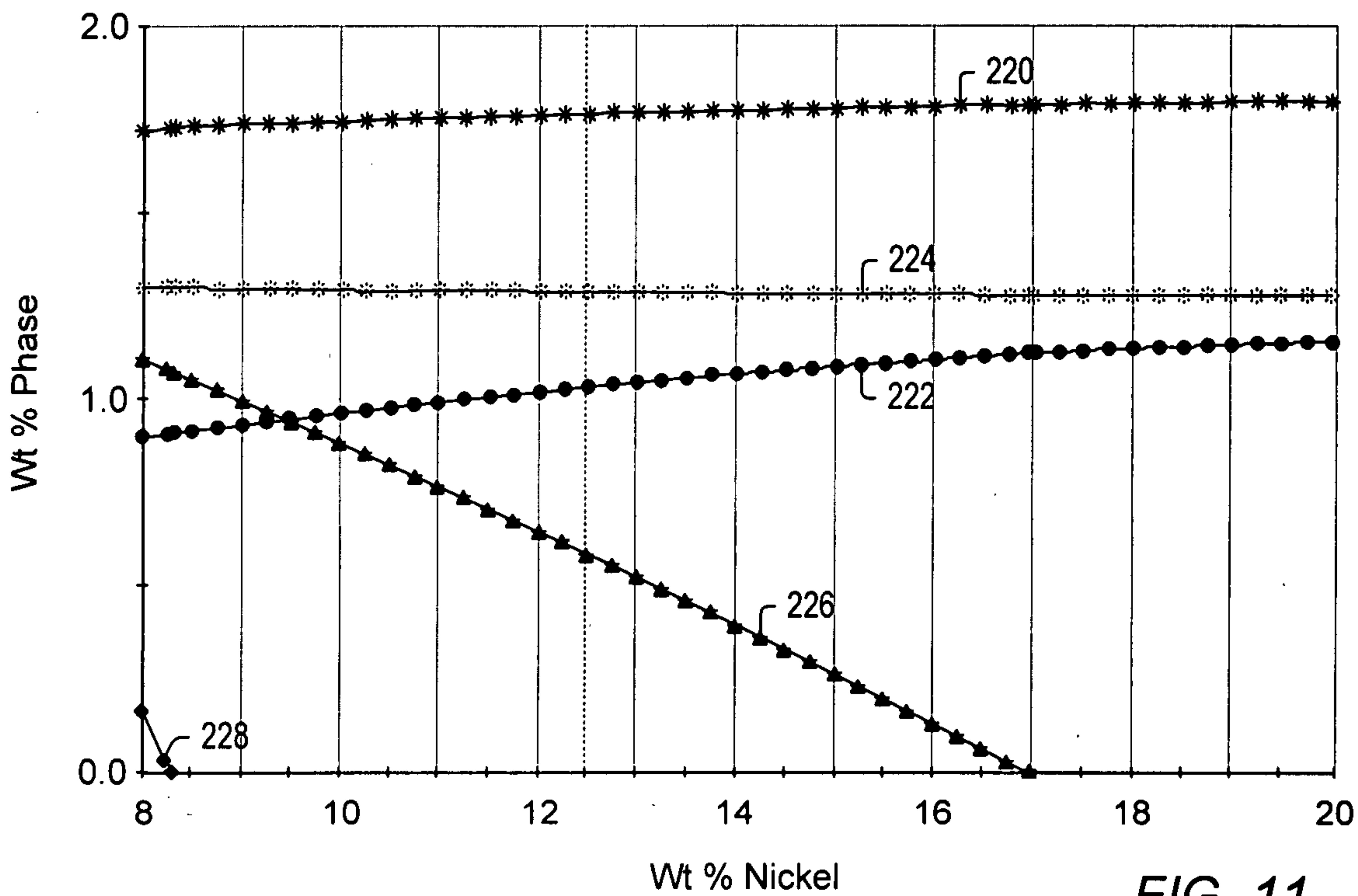
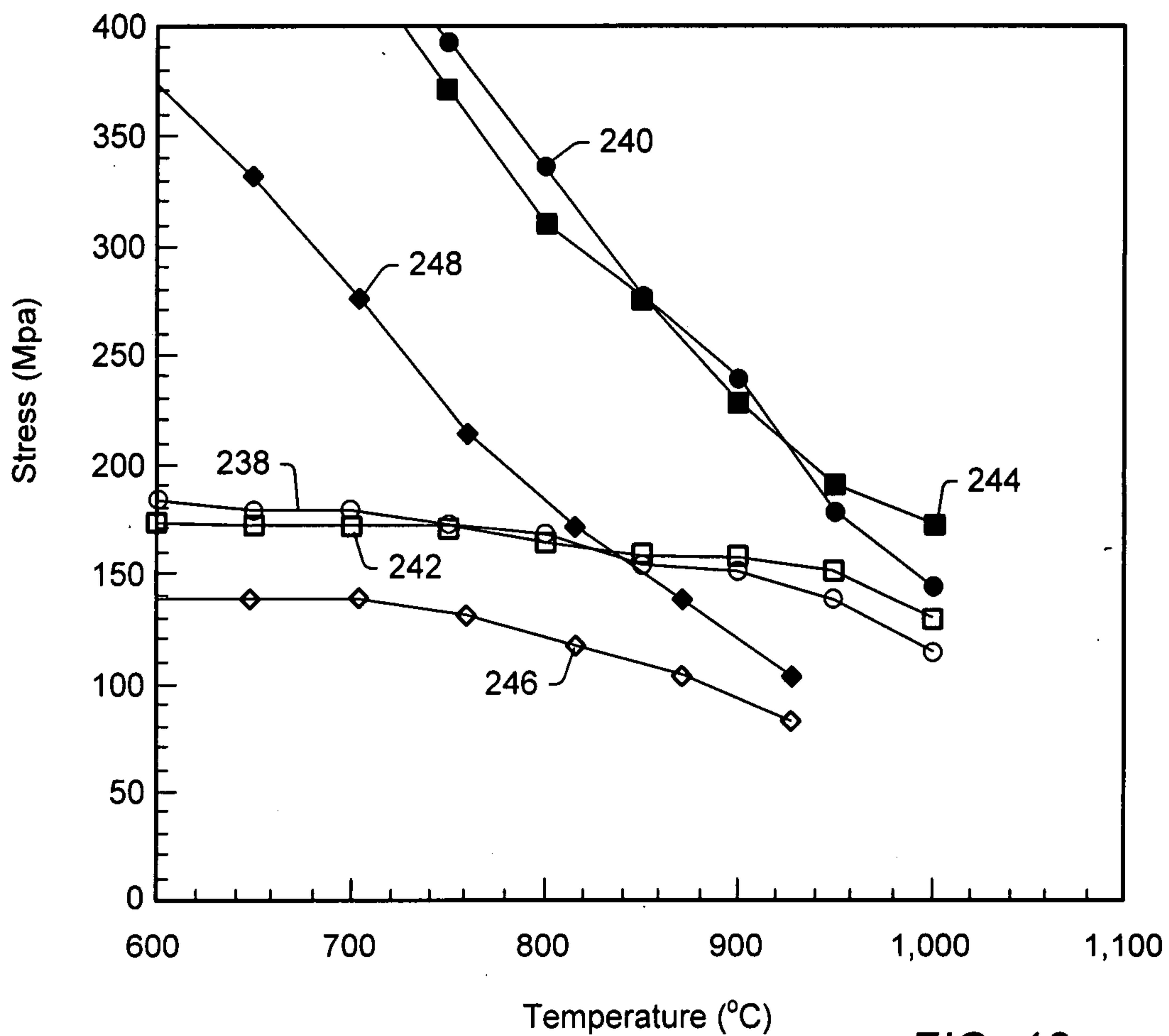
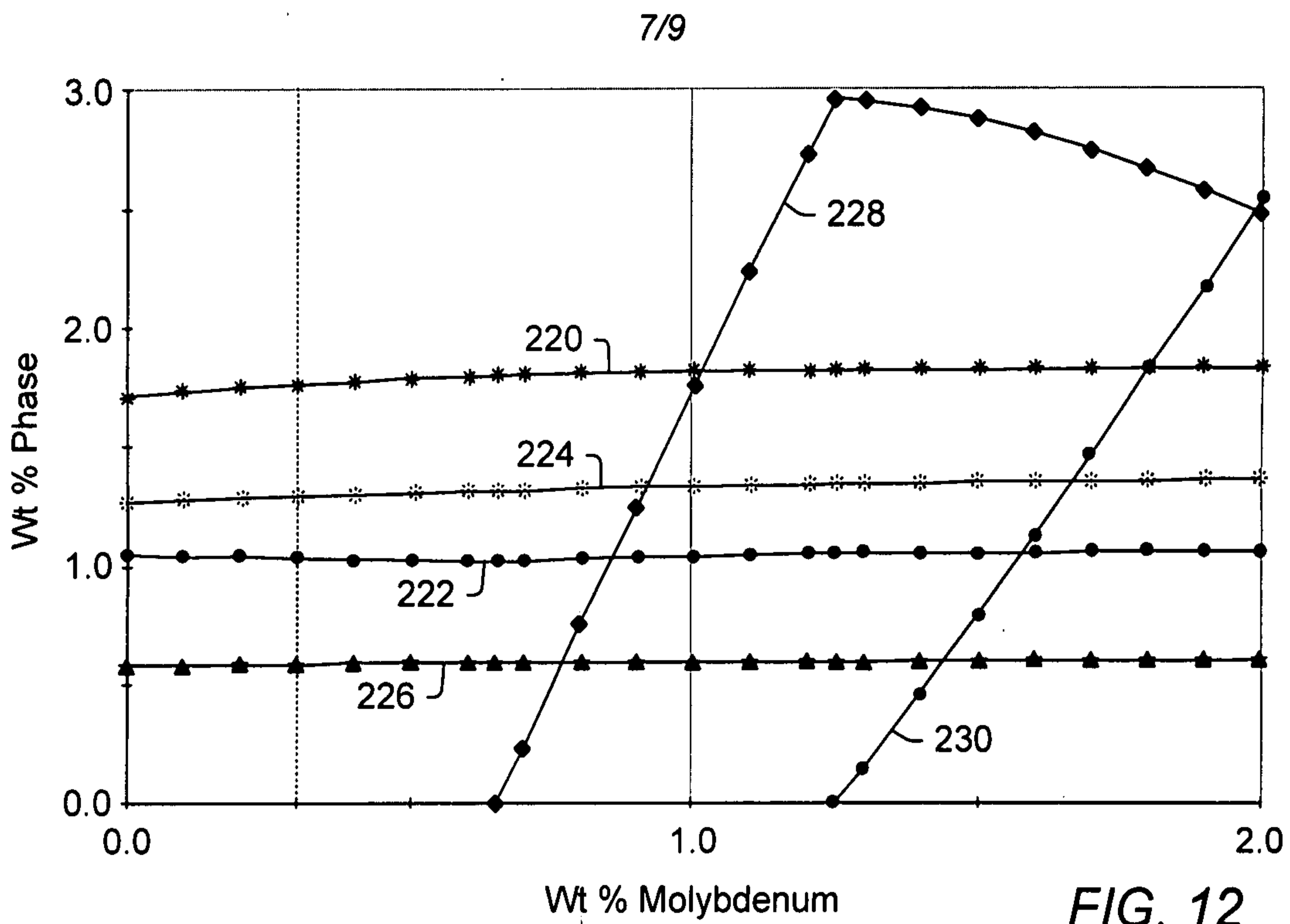


FIG. 11



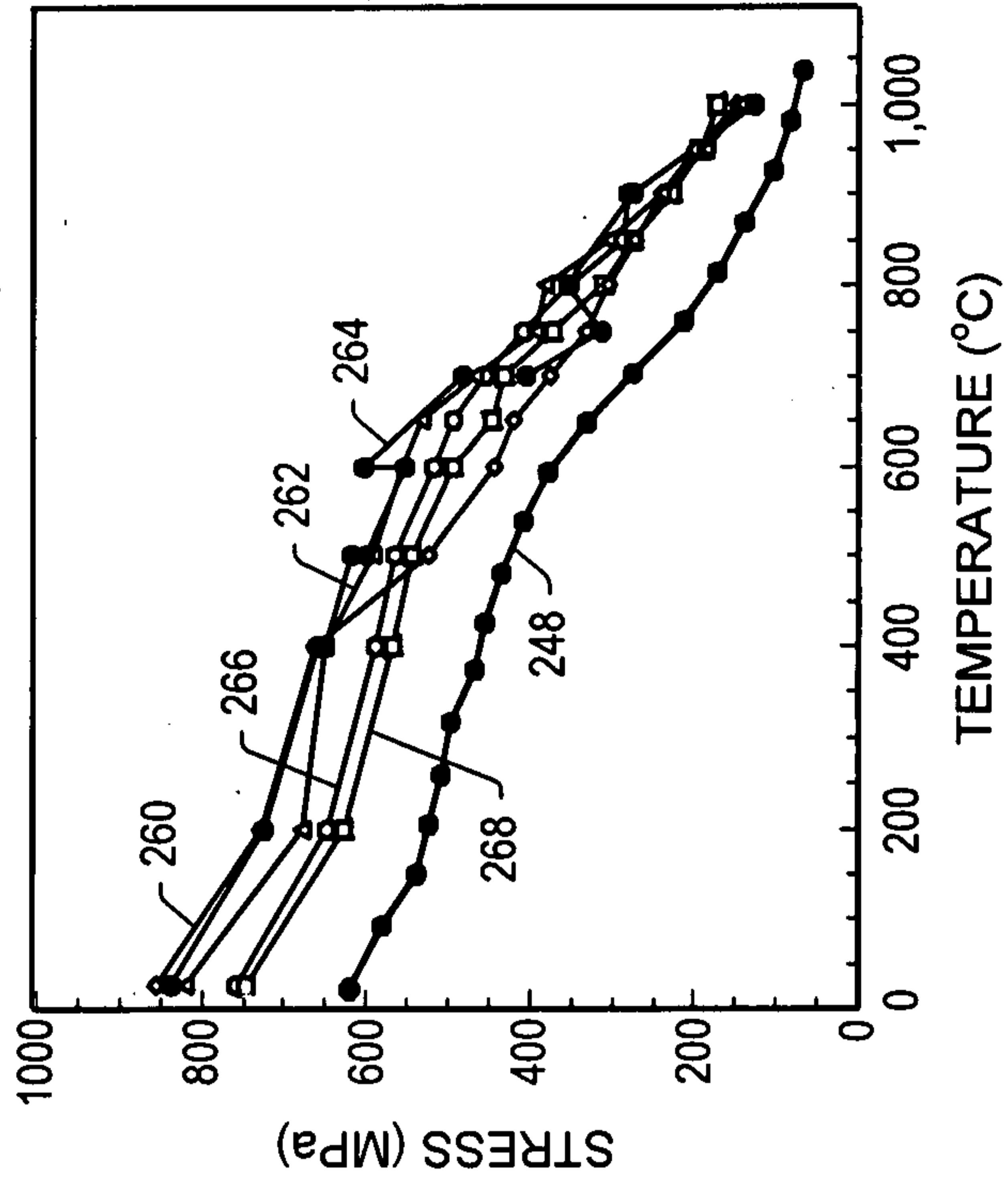


FIG. 15

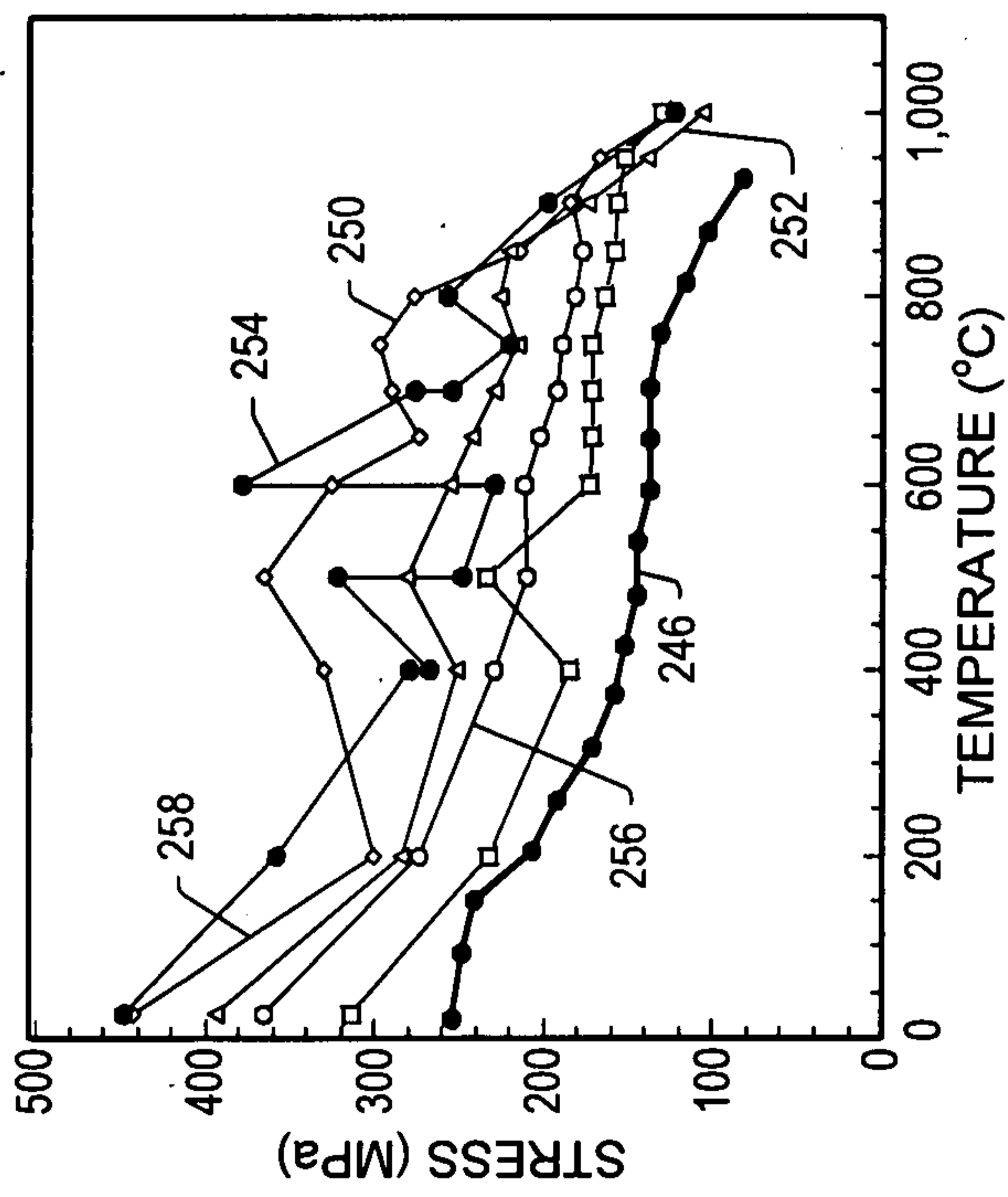


FIG. 14

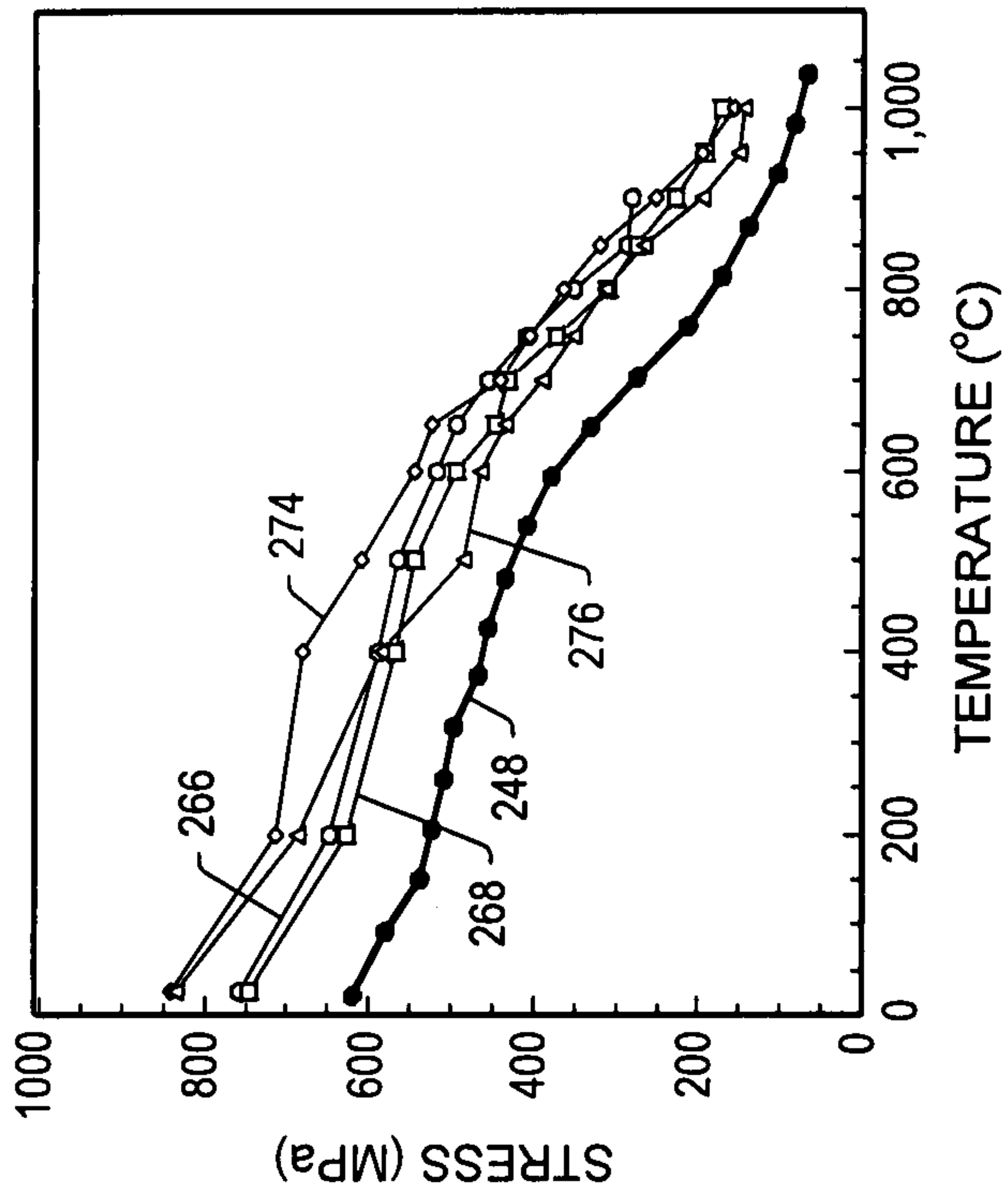


FIG. 17

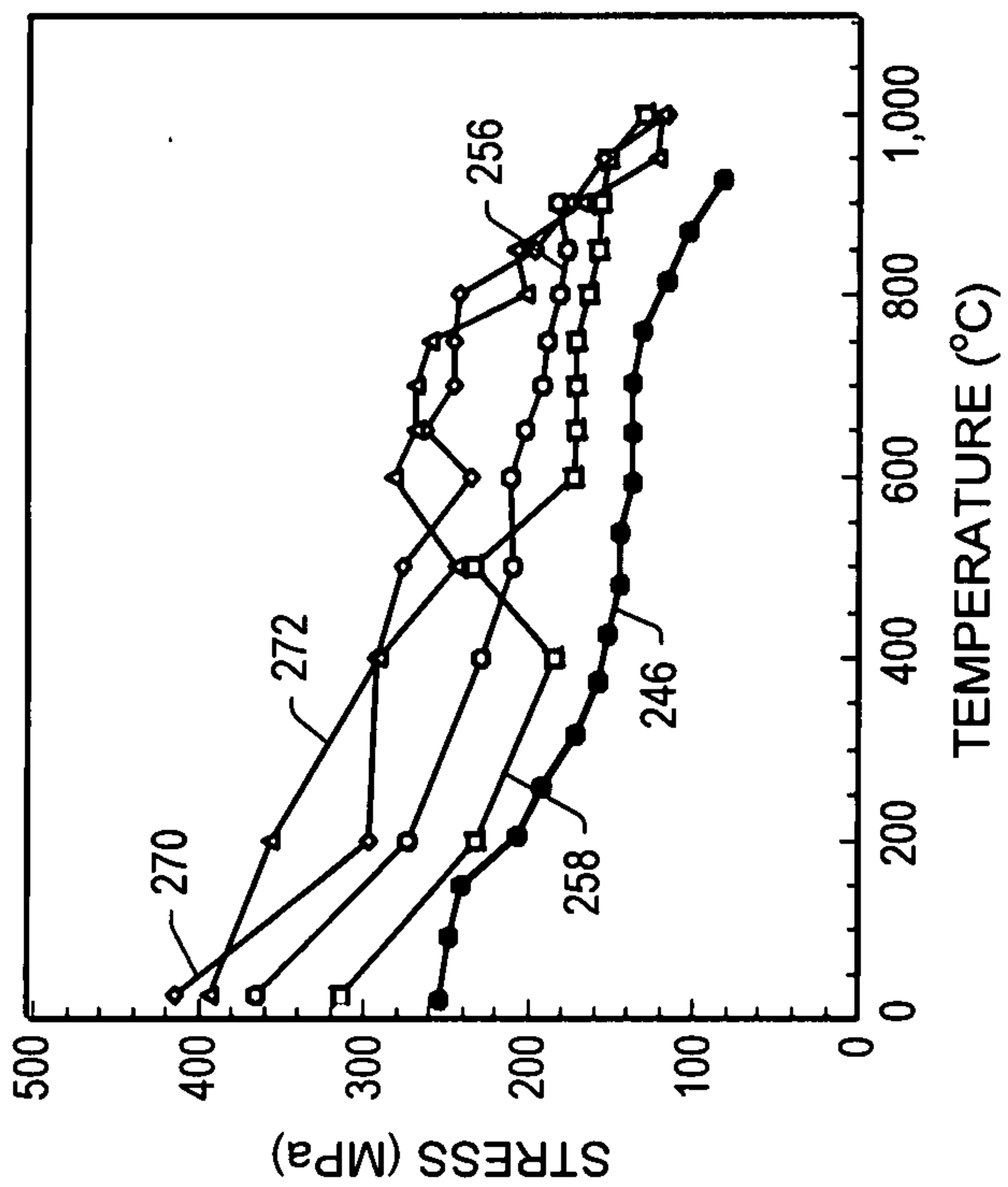


FIG. 16