(54) Title: THERMO-MECHANICAL PROCESSING OF NICKEL-TITANIUM ALLOYS

(57) Abstract: Processes for the production of nickel-titanium mill products are disclosed. A nickel-titanium alloy workpiece is cold worked at a temperature less than 500 C. The cold worked nickel-titanium alloy workpiece is hot isostatic pressed (HIP'ed).

TITLE

THERMO-MECHANICAL PROCESSING OF NICKEL-TITANIUM ALLOYS

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TECHNICAL FIELD

[0001]   This specification is directed to processes for producing nickel-titanium alloy mill products and to the mill products produced by the processes described in this specification.

BACKGROUND

[0002]   Equiatomic and near-equiatomic nickel-titanium alloys possess both "shape memory" and "superelastic" properties. More specifically, these alloys, which are commonly referred to as "Nitinol" alloys, are known to undergo a martensitic transformation from a parent phase (commonly referred to as the austenite phase) to at least one martensite phase on cooling to a temperature below the martensite start temperature ("M_s") of the alloy. This transformation is complete on cooling to the martensite finish temperature ("M_f") of the alloy. Further, the transformation is reversible when the material is heated to a temperature above its austenite finish temperature ("A_f").

[0003]   This reversible martensitic transformation gives rise to the shape memory properties of the alloys. For example, a nickel-titanium shape-memory alloy can be formed into a first shape while in the austenite phase (i.e., at a temperature above the A_f of the alloy), subsequently cooled to a temperature below the M_f, and deformed into a second shape. As long as the material remains below the austenite

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start temperature ("A_s") of the alloy (i.e., the temperature at which the transition to austenite begins), the alloy will retain the second shape. However, if the shape-memory alloy is heated to a temperature above the A_f, the alloy will revert back to the first shape if not physically constrained, or when constrained can exert a stress upon another

5   article. Recoverable strains of up to 8% are generally achievable with nickel-titanium alloys due to the reversible austenite-to-martensite thermally-induced transition, and hence the term "shape-memory."

[0004]   The transformation between the austenite and martensite phases also gives rise to the "pseudoelastic" or "superelastic" properties of shape-memory

10   nickel-titanium alloys. When a shape-memory nickel-titanium alloy is strained at a temperature above the A_f of the alloy but below the so-called martensite deformation temperature ("M_d"), the alloy can undergo a stress-induced transformation from the austenite phase to the martensite phase. The M_d is therefore defined as the temperature above which martensite cannot be stress-induced. When a stress is

15   applied to a nickel-titanium alloy at a temperature between A_f and M_d, after a small elastic deformation, the alloy yields to the applied stress through a transformation from austenite to martensite. This transformation, combined with the ability of the martensite phase to deform under the applied stress by movement of twinned boundaries without the generation of dislocations, permits a nickel-titanium alloy to absorb a large amount

20   of strain energy by elastic deformation without plastically (i.e., permanently) deforming. When the strain is removed, the alloy is able to revert back to its unstrained condition, and hence the term "pseudoelastic." Recoverable strains of up to 8% are generally achievable with nickel-titanium alloys due to the reversible austenite-to-martensite stress-induced transition, and hence the term "superelastic." Thus, superelastic nickel-

25   titanium alloys macroscopically appear to be very elastic relative to other alloys. The terms "pseudoelastic" and "superelastic" are synonymous when used in connection with nickel-titanium alloys, and the term "superelastic" is used in this specification.

[0005]   The ability to make commercial use of the unique properties of shape-memory and superelastic nickel-titanium alloys is dependent in part upon the

30   temperatures at which these transformations occur, i.e., the A_s, A_f, M_s, M_f, and M_d of the

alloy. For example, in applications such as vascular stents, vascular filters, and other medical devices, it is generally important that nickel-titanium alloys exhibit superelastic properties within the range of *in vivo* temperatures, *i.e.*, $A_f \leq$ ~37°C $\leq M_d$. It has been observed that the transformation temperatures of nickel-titanium alloys are highly

5   dependent on composition. For example, it has been observed that the transformation temperatures of nickel-titanium alloys can change more than 100 K for a 1 atomic percent change in composition of the alloys.

[0006]   In addition, various applications of nickel-titanium alloys, such as, for example, actuators and implantable stents and other medical devices, may be

10   considered to be fatigue critical. Fatigue refers to the progressive and localized structural damage that occurs when a material is subjected to cyclic loading. The repetitive loading and unloading causes the formation of microscopic cracks that may increase in size as a material is further subjected to cyclic loading at stress levels well below the material's yield strength, or elastic limit. Fatigue cracks may eventually reach

15   a critical size, resulting in the sudden failure of a material subjected to cyclic loading. It has been observed that fatigue cracks tend to initiate at non-metallic inclusions and other second phases in nickel-titanium alloys. Accordingly, various applications of nickel-titanium alloys, such as, for example, actuators, implantable stents, and other fatigue critical devices, may be considered to be inclusion and second phase critical.

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SUMMARY

[0007]   In a non-limiting embodiment, a process for the production of a nickel-titanium alloy mill product comprises cold working a nickel-titanium alloy workpiece at a temperature less than 500°C, and hot isostatic pressing (HIP'ing) the

25   cold worked nickel-titanium alloy workpiece.

[0008]   In another non-limiting embodiment, a process for the production of a nickel-titanium alloy mill product comprises hot working a nickel-titanium alloy workpiece at a temperature greater than or equal to 500°C and then cold working the

hot worked nickel-titanium alloy workpiece at a temperature less than 500°C. The cold worked nickel-titanium alloy workpiece is hot isostatic pressed (HIP'ed) for at least 0.25 hour in a HIP furnace operating at a temperature in the range of 700°C to 1000°C and a pressure in the range of 3,000 psi to 25,000 psi.

[0009]   In another non-limiting embodiment, a process for the production of a nickel-titanium alloy mill product comprises hot forging a nickel-titanium alloy ingot at a temperature greater than or equal to 500°C to produce a nickel-titanium alloy billet. The nickel-titanium alloy billet is hot bar rolled at a temperature greater than or equal to 500°C to produce a nickel-titanium alloy workpiece. The nickel-titanium alloy workpiece is cold drawn at a temperature less than 500°C to produce a nickel-titanium alloy bar. The cold worked nickel-titanium alloy bar is hot isostatic pressed for at least 0.25 hour in a HIP furnace operating at a temperature in the range of 700°C to 1000°C and a pressure in the range of 3,000 psi to 25,000 psi.

[0010]   It is understood that the invention disclosed and described in this specification is not limited to the embodiments summarized in this Summary.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]   Various features and characteristics of the non-limiting and non-exhaustive embodiments disclosed and described in this specification may be better understood by reference to the accompanying figures, in which:

[0012]   Figure 1 is an equilibrium phase diagram for binary nickel-titanium alloys;

[0013]   Figures 2A and 2B are schematic diagrams illustrating the effect of working on non-metallic inclusions and porosity in nickel-titanium alloy microstructure;

[0014]   Figure 3 is a scanning electron microscopy (SEM) image (500x magnification in backscatter electron mode) showing non-metallic inclusions and associated porosity in a nickel-titanium alloy;

[0015]   Figures 4A-4G are scanning electron microscopy images (500x magnification in backscatter electron mode) of nickel-titanium alloys processed in accordance with embodiments described in this specification;

[0016]   Figures 5A-5G are scanning electron microscopy images (500x magnification in backscatter electron mode) of nickel-titanium alloys processed in accordance with embodiments described in this specification;

[0017]   Figures 6A-6H are scanning electron microscopy images (500x magnification in backscatter electron mode) of nickel-titanium alloys processed in accordance with embodiments described in this specification;

[0018]   Figures 7A-7D are scanning electron microscopy images (500x magnification in backscatter electron mode) of nickel-titanium alloys processed in accordance with embodiments described in this specification; and

[0019]   Figures 8A-8E are scanning electron microscopy images (500x magnification in backscatter electron mode) of nickel-titanium alloys processed in accordance with embodiments described in this specification.

[0020]   The reader will appreciate the foregoing details, as well as others, upon considering the following detailed description of various non-limiting and non-exhaustive embodiments according to this specification.

DESCRIPTION

[0021]   Various embodiments are described and illustrated in this specification to provide an overall understanding of the function, operation, and implementation of the disclosed processes for the production of nickel-titanium alloy mill products. It is understood that the various embodiments described and illustrated in this specification are non-limiting and non-exhaustive. Thus, the invention is not necessarily limited by the description of the various non-limiting and non-exhaustive embodiments disclosed in this specification. The features and characteristics illustrated and/or described in connection with various embodiments may be combined with the features

and characteristics of other embodiments. Such modifications and variations are intended to be included within the scope of this specification. As such, the claims may be amended to recite any features or characteristics expressly or inherently described in, or otherwise expressly or inherently supported by, this specification. Further, the

5   Applicant(s) reserve the right to amend the claims to affirmatively disclaim features or characteristics that may be present in the prior art. Therefore, any such amendments comply with the requirements of 35 U.S.C. §§ 112(a) and 132(a). The various embodiments disclosed and described in this specification can comprise, consist of, or consist essentially of the features and characteristics as variously described in this

10   specification.

[0022]   Also, any numerical range recited in this specification is intended to include all sub-ranges of the same numerical precision subsumed within the recited range. For example, a range of "1.0 to 10.0" is intended to include all sub-ranges between (and including) the recited minimum value of 1.0 and the recited maximum

15   value of 10.0, that is, having a minimum value equal to or greater than 1.0 and a maximum value equal to or less than 10.0, such as, for example, 2.4 to 7.6. Any maximum numerical limitation recited in this specification is intended to include all lower numerical limitations subsumed therein and any minimum numerical limitation recited in this specification is intended to include all higher numerical limitations subsumed

20   therein. Accordingly, the Applicant(s) reserve the right to amend this specification, including the claims, to expressly recite any sub-range subsumed within the ranges expressly recited herein. All such ranges are intended to be inherently described in this specification such that amending to expressly recite any such sub-ranges would comply with the requirements of 35 U.S.C. §§ 112(a) and 132(a).

25   [0023]   Any patent, publication, or other disclosure material identified herein is incorporated by reference into this specification in its entirety unless otherwise indicated, but only to the extent that the incorporated material does not conflict with existing descriptions, definitions, statements, or other disclosure material expressly set forth in this specification. As such, and to the extent necessary, the express disclosure

30   as set forth in this specification supersedes any conflicting material incorporated by

reference herein. Any material, or portion thereof, that is said to be incorporated by reference into this specification, but which conflicts with existing definitions, statements, or other disclosure material set forth herein, is only incorporated to the extent that no conflict arises between that incorporated material and the existing disclosure material.

5   Applicants reserve the right to amend this specification to expressly recite any subject matter, or portion thereof, incorporated by reference herein.

[0024]   The grammatical articles "one", "a", "an", and "the", as used in this specification, are intended to include "at least one" or "one or more", unless otherwise indicated. Thus, the articles are used in this specification to refer to one or more than

10   one (*i.e.*, to "at least one") of the grammatical objects of the article. By way of example, "a component" means one or more components, and thus, possibly, more than one component is contemplated and may be employed or used in an implementation of the described embodiments. Further, the use of a singular noun includes the plural, and the use of a plural noun includes the singular, unless the context of the usage requires

15   otherwise.

[0025]   Various embodiments described in this specification are directed to processes for producing a nickel-titanium alloy mill product having improved microstructure such as, for example, reduced area fraction and size of non-metallic inclusions and porosity. As used herein, the term "mill product" refers to alloy articles

20   produced by thermo-mechanical processing of alloy ingots. Mill products include, but are not limited to, billets, bars, rods, wire, tubes, slabs, plates, sheets, and foils. Also, as used herein, the term "nickel-titanium alloy" refers to alloy compositions comprising at least 35% titanium and at least 45% nickel based on the total weight of the alloy composition. In various embodiments, the processes described in this specification are

25   applicable to near-equiatomic nickel-titanium alloys. As used herein, the term "near-equiatomic nickel-titanium alloy" refers to alloys comprising 45.0 atomic percent to 55.0 atomic percent nickel, balance titanium and residual impurities. Near-equiatomic nickel-titanium alloys include equiatomic binary nickel-titanium alloys consisting essentially of 50% nickel and 50% titanium, on an atomic basis.

[0026]   Nickel-titanium alloy mill products may be made from processes that comprise, for example: formulating the alloy chemistry using a melting technique such as vacuum induction melting (VIM) and/or vacuum arc remelting (VAR); casting a nickel-titanium alloy ingot; forging the cast ingot into a billet; hot working the billet to a mill stock form; cold working (with optional intermediate anneals) the mill stock form to a mill product form; and mill annealing the mill product form to produce a final mill product. These processes may produce mill products that have variable microstructural characteristics such as microcleanliness. As used herein, the term "microcleanliness" refers to the non-metallic inclusion and porosity characteristics of a nickel-titanium alloy as defined in section 9.2 of ASTM F 2063 – 12: *Standard Specification for Wrought Nickel-Titanium Shape Memory Alloys for Medical Devices and Surgical Implants*, which is incorporated by reference into this specification. For producers of nickel-titanium alloy mill products, it may be commercially important to produce nickel-titanium alloy mill products that consistently meet the microcleanliness and other requirements of industry standards such as the ASTM F 2063 – 12 specification.

[0027]   The processes described in this specification comprise cold working a nickel-titanium alloy workpiece at a temperature less than 500°C, and hot isostatic pressing the cold worked nickel-titanium alloy workpiece. The cold working reduces the size and the area fraction of non-metallic inclusions in the nickel-titanium alloy workpiece. The hot isostatic pressing reduces or eliminates the porosity in the nickel-titanium alloy workpiece.

[0028]   In general, the term "cold working" refers to working an alloy at a temperature below that at which the flow stress of the material is significantly diminished. As used herein in connection with the disclosed processes, "cold working," "cold worked," "cold forming," "cold rolling," and like terms (or "cold" used in connection with a particular working or forming technique, *e.g.*, "cold drawing") refer to working or the state of having been worked, as the case may be, at a temperature less than 500°C. Cold working operations may be performed when the internal and/or the surface temperature of a workpiece is less than 500°C. Cold working operations may be performed at any temperature less than 500°C, such as, for example, less than 400°C,

less than 300°C, less than 200°C, or less than 100°C. In various embodiments, cold

working operations may be performed at ambient temperature. In a given cold working

operation, the internal and/or surface temperature of a nickel-titanium alloy workpiece

may increase above a specified limit (e.g., 500°C or 100°C) during the working due to

5   adiabatic heating; however, for purposes of the processes described in this

specification, the operation is still a cold working operation.

[0029]   In general, hot isostatic pressing (HIP or HIP'ing) refers to the

isostatic (i.e., uniform) application of a high pressure and high temperature gas, such

as, for example, argon, to the external surfaces of a workpiece in a HIP furnace. As

10   used herein in connection with the disclosed processes, "hot isostatic pressing," "hot

isostatic pressed," and like terms or acronyms refer to the isostatic application of a high

pressure and high temperature gas to a nickel-titanium alloy workpiece in a cold worked

condition. In various embodiments, a nickel-titanium alloy workpiece may be hot

isostatic pressed in a HIP furnace operating at a temperature in the range of 700°C to

15   1000°C and a pressure in the range of 3,000 psi to 50,000 psi. In some embodiments,

a nickel-titanium alloy workpiece may be hot isostatic pressed in a HIP furnace

operating at a temperature in the range of 750°C to 950°C, 800°C to 950°C, 800°C to

900°C, or 850°C to 900°C; and at a pressure in the range of 7,500 psi to 50,000 psi,

10,000 psi to 45,000 psi, 10,000 psi to 25,000 psi, 10,000 psi to 20,000 psi, 10,000 psi

20   to 17,000 psi, 12,000 psi to 17,000 psi, or 12,000 psi to 15,000 psi. In various

embodiments, a nickel-titanium alloy workpiece may be hot isostatic pressed in a HIP

furnace for at least 0.25 hour, and in some embodiments, for at least 0.5 hour, 0.75

hour. 1.0 hour, 1.5 hours, or at least 2.0 hours, at temperature and pressure.

[0030]   As used herein, the term "non-metallic inclusions" refers to

25   secondary phases in a NiTi metallic matrix comprising non-metal constituents such as

carbon and/or oxygen atoms. Non-metallic inclusions include both $Ti_4Ni_2O_x$ oxide non-

metallic inclusions and titanium carbide (TiC) and/or titanium oxy-carbide (Ti(C,O)) non-

metallic inclusions. Non-metallic inclusions do not include discrete inter-metallic

phases, such as, Ni_4Ti_3, Ni_3Ti_2, Ni_3Ti, and Ti_2Ni, which may also form in near-equiatomic

30   nickel-titanium alloys.

[0031]   An equiatomic nickel-titanium alloy consisting essentially of 50%
nickel and 50% titanium, on an atomic basis (approximately 55% Ni, 45% Ti, by weight),
has an austenite phase consisting essentially of a NiTi B2 cubic structure (*i.e.*, a cesium
chloride type structure). The martensitic transformations associated with the shape-
5   memory effect and superelasticity are diffusionless, and the martensite phase has a
B19' monoclinic crystal structure. The NiTi phase field is very narrow and essentially
corresponds to equiatomic nickel-titanium at temperatures below about 650°C. See
Figure 1. The boundary of the NiTi phase field on the Ti-rich side is essentially vertical
from ambient temperature up to about 600°C. The boundary of the NiTi phase field on
10   the Ni-rich side decreases with deceasing temperature, and the solubility of nickel in B2
NiTi is negligible at about 600°C and below. Therefore, near-equiatomic nickel-titanium
alloys generally contain inter-metallic second phases (*e.g.*, Ni_4Ti_3, Ni_3Ti_2, Ni_3Ti, and
Ti_2Ni), the chemical identity of which depends upon whether a near-equiatomic nickel-
titanium alloy is Ti-rich or Ni-rich.

15   [0032]   As previously described, nickel-titanium alloy ingots may be cast
from molten alloy melted using vacuum induction melting (VIM). A titanium input
material and a nickel input material may be placed in a graphite crucible in a VIM
furnace and melted to produce the molten nickel-titanium alloy. During melting, carbon
from the graphite crucible may dissolve into the molten alloy. During casting of a nickel-
20   titanium alloy ingot, the carbon may react with the molten alloy to produce cubic titanium
carbide (TiC) and/or cubic titanium oxy-carbide (Ti(C,O)) particles that form non-metallic
inclusions in the cast ingot. VIM ingots may generally contain 100-800 ppm carbon by
weight and 100-400 ppm oxygen by weight, which may produce relatively large non-
metallic inclusions in the nickel-titanium alloy matrix.

25   [0033]   Nickel-titanium alloy ingots may also be produced from molten alloy
melted using vacuum arc remelting (VAR). In this regard, the term VAR may be a
misnomer because the titanium input material and the nickel input material may be
melted together to form the alloy composition in the first instance in a VAR furnace, in
which case the operation may be more accurately termed vacuum arc melting. For
30   consistency, the terms "vacuum arc remelting" and "VAR" are used in this specification

to refer to both alloy remelting and initial alloy melting from elemental input materials or other feed materials, as the case may be in a given operation.

[0034]   A titanium input material and a nickel input material may be used to mechanically form an electrode that is vacuum arc remelted into a water-cooled copper
5   crucible in a VAR furnace. The use of a water-cooled copper crucible may significantly reduce the level of carbon pickup relative to nickel-titanium alloy melted using VIM, which requires a graphite crucible. VAR ingots may generally contain less than 100 ppm carbon by weight, which significantly reduces or eliminates the formation of titanium carbide (TiC) and/or titanium oxy-carbide (Ti(C,O)) non-metallic inclusions.
10   However, VAR ingots may generally contain 100-400 ppm oxygen by weight when produced from titanium sponge input material, for example. The oxygen may react with the molten alloy to produce $Ti_4Ni_2O_x$ oxide non-metallic inclusions, which have nearly the same cubic structure (space group Fd3m) as a Ti_2Ni intermetallic second phase generally present in Ti-rich near-equiatomic nickel-titanium alloys, for example. These
15   non-metallic oxide inclusions have even been observed in high purity VAR ingots melted from low-oxygen (<60 ppm by weight) iodide-reduced titanium crystal bar.

[0035]   Cast nickel-titanium alloy ingots and articles formed from the ingots may contain relatively large non-metallic inclusions in the nickel-titanium alloy matrix. These large non-metallic inclusion particles may adversely affect the fatigue life and
20   surface quality of nickel-titanium alloy articles, particularly near-equiatomic nickel-titanium alloy articles. In fact, industry-standard specifications place strict limits on the size and area fraction of non-metallic inclusions in nickel-titanium alloys intended for use in fatigue-critical and surface quality-critical applications such as, for example, actuators, implantable stents, and other medical devices. See ASTM F 2063 – 12:
25   Standard Specification for Wrought Nickel-Titanium Shape Memory Alloys for Medical Devices and Surgical Implants, which is incorporated by reference into this specification. Therefore, it may be important to minimize the size and area fraction of non-metallic inclusions in nickel-titanium alloy mill products.

[0036]   The non-metallic inclusions that form in cast nickel-titanium alloys
30   are generally friable and break-up and move during working of the material. The break-

up, elongation, and movement of the non-metallic inclusions during working operations decreases the size of non-metallic inclusions in nickel-titanium alloys. However, the break-up and movement of the non-metallic inclusions during working operations may also simultaneously cause the formation of microscopic voids that increase the porosity in the bulk material. This phenomenon is shown in Figures 2A and 2B, which schematically illustrate the counter-effects of working on non-metallic inclusions and porosity in nickel-titanium alloy microstructure. Figure 2A illustrates the microstructure of a nickel-titanium alloy comprising non-metallic inclusions 10 but lacking porosity. Figure 2B illustrates the effect of working on the non-metallic inclusions 10', which are shown broken-up into smaller particles and separated, but with increased porosity 20 interconnecting the smaller inclusion particles. Figure 3 is an actual scanning electron microscopy (SEM) image (500x in backscatter electron mode) showing a non-metallic inclusion and associated porosity voids in a nickel-titanium alloy.

[0037]   Like non-metallic inclusions, porosity in nickel-titanium alloys can adversely affect the fatigue life and surface quality of nickel-titanium alloy products. In fact, industry-standard specifications also place strict limits on the porosity in nickel-titanium alloys intended for use in fatigue-critical and surface quality-critical applications such as, for example, actuators, implantable stents, and other medical devices. See ASTM F 2063 – 12: *Standard Specification for Wrought Nickel-Titanium Shape Memory Alloys for Medical Devices and Surgical Implants.*

[0038]   Specifically, in accordance with the ASTM F 2063 – 12 specification, for near-equiatomic nickel-titanium alloys having an A_s less than or equal to 30°C, the maximum allowable length dimension of porosity and non-metallic inclusions is 39.0 micrometers (0.0015 inch), wherein the length includes contiguous particles and voids, and particles separated by voids. Additionally, porosity and non-metallic inclusions cannot constitute more than 2.8% (area percent) of a nickel-titanium alloy microstructure as viewed at 400x to 500x magnification in any field of view. These measurements may be made in accordance with ASTM E1245 – 03 (2008) – *Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals*

by Automatic Image Analysis, which is incorporated by reference into this specification, or an equivalent method.

[0039]   Referring to Figures 2A and 2B, while working a nickel-titanium alloy may decrease the size of non-metallic inclusions, the net result may be to increase the total size and area fraction of non-metallic inclusions combined with porosity. Therefore, the consistent and efficient production of nickel-titanium alloy material that meets the strict limits of industry standards, such as the ASTM F 2063 – 12 specification, has proven to be a challenge to the producers of nickel-titanium alloy mill products. The processes described in this specification meet that challenge by providing nickel-titanium alloy mill products having improved microstructure, including reduced size and area fraction of both non-metallic inclusions and porosity. For example, in various embodiments, the nickel-titanium alloy mill products produced by the processes described in this specification meet the size and area fraction requirements of the ASTM F 2063 – 12 standard specification, only measured after cold working.

[0040]   As previously described, a process for the production of a nickel-titanium alloy mill product may comprise cold working and hot isostatic pressing a nickel-titanium alloy workpiece. The cold working of a nickel-titanium alloy workpiece at a temperature less than 500°C, such as at ambient temperature, for example, effectively breaks-up and moves non-metallic inclusions along the direction of the applied cold work and reduces the size of the non-metallic inclusions in the nickel-titanium alloy workpiece. The cold working may be applied to a nickel-titanium alloy workpiece after any final hot working operations have been completed. In general, "hot working" refers to working an alloy at a temperature above that at which the flow stress of the material is significantly diminished. As used herein in connection with the described processes, "hot working," "hot worked," "hot forging," "hot rolling," and like terms (or "hot" used in connection with a particular working or forming technique) refer to working, or the state of having been worked, as the case may be, at a temperature greater than or equal to 500°C.

[0041]   In various embodiments, a process for the production of a nickel-titanium alloy mill product may comprise a hot working operation before the cold working operation. As described above, nickel-titanium alloys may be cast from nickel and titanium input materials using VIM and/or VAR to produce nickel-titanium alloy

5   ingots. The cast nickel-titanium alloy ingots may be hot worked to produce a billet. For example, in various embodiments, a cast nickel-titanium alloy ingot (workpiece) having a diameter in the range of 10.0 inches to 30.0 inches may be hot worked (e.g., by hot rotary forging) to produce a billet having a diameter in the range of 2.5 inches to 8.0 inches. Nickel-titanium alloy billets (workpieces) may be hot bar rolled, for example, to

10   produce rod or bar stock having a diameter in the range of 0.218 inches to 3.7 inches. Nickel-titanium alloy rod or bar stock (workpieces) may be hot drawn, for example, to produce nickel-titanium alloy rods, bars, or wire having a diameter in the range of 0.001 inches to 0.218 inches. Following any hot working operations, a nickel-titanium alloy mill product (in an intermediate form) may be cold worked in accordance with

15   embodiments described in this specification to produce the final macrostructural form of a nickel-titanium alloy mill product. As used herein, the terms "macrostructure" or "macrostructural" refer to the macroscopic shape and dimensions of an alloy workpiece or mill product, in contrast to "microstructure," which refers to the microscopic grain structure and phase structure of an alloy material (including inclusions and porosity).

20   [0042]   In various embodiments, cast nickel-titanium alloy ingots may be hot worked using forming techniques including, but not limited to, forging, upsetting, drawing, rolling, extruding, pilgering, rocking, swaging, heading, coining, and combinations of any thereof. One or more hot working operations may be used to convert a cast nickel-titanium alloy ingot into a semi-finished or intermediate mill product

25   (workpiece). The intermediate mill product (workpiece) may be subsequently cold worked into a final macrostructural form for the mill product using one or more cold working operations.   The cold working may comprise forming techniques including, but not limited to, forging, upsetting, drawing, rolling, extruding, pilgering, rocking, swaging, heading, coining, and combinations of any thereof. In various embodiments, a nickel-

30   titanium alloy workpiece (e.g., an ingot, a billet, or other mill product stock form) may be hot worked using at least one hot working technique and subsequently cold worked

using at least one cold working technique. In various embodiments, hot working may be performed on a nickel-titanium alloy workpiece at an initial internal or surface temperature in the range of 500°C to 1000°C, or any sub-range subsumed therein, such as, for example, 600°C to 900°C or 700°C to 900°C. In various embodiments, cold

5   working may be performed on a nickel-titanium alloy article at an initial internal or surface temperature less than 500°C such as ambient temperature, for example.

[0043]   By way of example, a cast nickel-titanium alloy ingot may be hot forged to produce a nickel-titanium alloy billet. The nickel-titanium alloy billet may be hot bar rolled, for example, to produce nickel-titanium alloy round bar stock having a

10   diameter larger than a specified final diameter for a bar or rod mill product. The larger diameter nickel-titanium alloy round bar stock may be a semi-finished mill product or intermediate workpiece that is subsequently cold drawn, for example, to produce a bar or rod mill product having a final specified diameter. The cold working of the nickel-titanium alloy workpiece may break-up and move non-metallic inclusions along the

15   drawing direction and reduce the size of the non-metallic inclusions in the workpiece. The cold working may also increase the porosity in the nickel-titanium alloy workpiece, adding to any porosity present in the workpiece resulting from the prior hot working operations. A subsequent hot isostatic pressing operation may reduce or completely eliminate the porosity in the nickel-titanium alloy workpiece. A subsequent hot isostatic

20   pressing operation may also simultaneously recrystallize the nickel-titanium alloy workpiece and/or provide a stress relief anneal to the workpiece.

[0044]   Nickel-titanium alloys exhibit rapid cold work hardening and, therefore, cold worked nickel-titanium alloy articles may be annealed after successive cold working operations. For example, a process for producing a nickel-titanium alloy

25   mill product may comprise cold working a nickel-titanium alloy workpiece in a first cold working operation, annealing the cold worked nickel-titanium alloy workpiece, cold working the annealed nickel-titanium alloy workpiece in a second cold working operation, and hot isostatic pressing the twice cold worked nickel-titanium alloy workpiece. After the second cold working operation and before the hot isostatic

30   pressing operation, the nickel-titanium alloy workpiece may be subjected to at least one

additional annealing operation, and at least one additional cold working operation. The number of successive cycles of intermediate annealing and cold working between a first cold working operation and a hot isostatic pressing operation may be determined by the amount of cold work to be put into the workpiece and the work hardening rate of the particular nickel-titanium alloy composition. Intermediate anneals between successive cold working operations may be performed in a furnace operating at a temperature in the range of 700°C to 900°C or 750°C to 850°C. Intermediate anneals between successive cold working operations may be performed for at least 20 seconds up to 2 hours or more furnace time, depending on the size of the material and the type of furnace.

[0045]   In various embodiments, hot working and/or cold working operations may be performed to produce the final macrostructural form of a nickel-titanium alloy mill product, and a subsequent hot isostatic pressing operation may be performed on the cold worked workpiece to produce the final microstructural form of the nickel-titanium alloy mill product. Unlike the use of hot isostatic pressing for the consolidation and sintering of metallurgical powders, the use of hot isostatic pressing in the processes described in this specification does not cause a macroscopic dimensional or shape change in the cold worked nickel-titanium alloy workpiece.

[0046]   While not intending to be bound by theory, it is believed that cold working is significantly more effective than hot working at breaking-up and moving the friable (i.e., hard and non-ductile) non-metallic inclusions in nickel-titanium alloys, which decreases the sizes of the non-metallic inclusions. During working operations, the strain energy input into the nickel-titanium alloy material causes the larger non-metallic inclusions to fracture into smaller inclusions that move apart in the direction of the strain. During hot working at elevated temperatures, the plastic flow stress of the nickel-titanium alloy material is significantly lower; therefore, the material more easily flows around the inclusions and does not impart as much strain energy into the inclusions to cause fracture and movement. However, during hot working, the plastic flow of the alloy material relative to the inclusions still creates void spaces between the inclusions and the nickel-titanium alloy material, thereby increasing the porosity of the material. On the

other hand, during cold working, the plastic flow stress of the nickel-titanium alloy material is significantly greater and the material does not plastically flow around the inclusions as readily. Therefore, significantly more strain energy is imparted to the inclusions to cause fracture and movement, which significantly increases the rate of

5   inclusion fracture, movement, size reduction, and area reduction, but also increases the rate of void formation and porosity. As previously described, however, while working a nickel-titanium alloy may decrease the size and area fraction of non-metallic inclusions, the net result may be to increase the total size and area fraction of non-metallic inclusions combined with porosity.

10   [0047]   The inventors have found that hot isostatic pressing a hot worked and/or cold worked nickel-titanium alloy workpiece will effectively close (*i.e.*, "heal") the porosity formed in the alloy during hot working and/or cold working operations. The hot isostatic pressing causes the alloy material to plastically yield on a microscopic scale and close the void spaces that form the internal porosity in nickel-titanium alloys. In this

15   manner, the hot isostatic pressing allows for micro-creep of the nickel-titanium alloy material into the void spaces. In addition, because the inside surfaces of the porosity voids have not been exposed to atmosphere, a metallurgical bond is created when the surfaces come together from the pressure of the HIP operation. This results in decreased size and area fraction of the non-metallic inclusions, which are separated by

20   nickel-titanium alloy material instead of void spaces. This is particularly advantageous for the production of nickel-titanium alloy mill products that meet the size and area fraction requirements of the ASTM F 2063 – 12 standard specification, measured after cold working, which sets strict limits on the aggregate size and area fraction of contiguous non-metallic inclusions and porosity voids (maximum allowable length

25   dimension of 39.0 micrometers (0.0015 inch), and maximum area fraction of 2.8%).

          [0048]   In various embodiments, a hot isostatic pressing operation may serve multiple functions. For example, a hot isostatic pressing operation may reduce or eliminate porosity in hot worked and/or cold worked nickel-titanium alloys, and the hot isostatic pressing operation may simultaneously anneal the nickel-titanium alloy,

30   thereby relieving any internal stresses induced by the prior cold working operations and,

in some embodiments, recrystallizing the alloy to achieve a desired grain structure such as, for example, an ASTM grain size number (G) of 4 or larger (as measured in accordance with ASTM E112 – 12: *Standard Test Methods for Determining Average Grain Size*, which is incorporated by reference into this specification). In various
5   embodiments, after the hot isostatic pressing, a nickel-titanium alloy mill product may be subjected to one or more finishing operations including, but not limited to, peeling, polishing, centerless grinding, blasting, pickling, straightening, sizing, honing, or other surface conditioning operations.

[0049]   In various embodiments, the mill products produced by the
10   processes described in this specification may comprise, for example, a billet, a bar, a rod, a tube, a slab, a plate, a sheet, a foil, or a wire.

[0050]   In various embodiments, a nickel input material and a titanium input material may be vacuum arc remelted to produce a nickel-titanium alloy VAR ingot that is hot worked and/or cold worked and hot isostatic pressed in accordance with the
15   embodiments described in this specification. The nickel input material may comprise electrolytic nickel or nickel powder, for example, and the titanium input material may be selected from the group consisting of titanium sponge, electrolytic titanium crystals, titanium powders, and iodide-reduced titanium crystal bar. The nickel input material and/or the titanium input material may comprise less pure forms of elemental nickel or
20   titanium that have been refined, for example, by electron beam melting before the nickel input material and the titanium input material are alloyed together to form the nickel-titanium alloy. Alloying elements in addition to nickel and titanium, if present, may be added using elemental input materials known in the metallurgical arts. The nickel input material and the titanium input material (and any other intentional alloying input
25   materials) may be mechanically compacted together to produce an input electrode for an initial VAR operation.

[0051]   The initial near-equiatomic nickel-titanium alloy composition may be melted as accurately as possible to a predetermined composition (such as, for example, 50.8 atomic percent (approximately 55.8 weight percent) nickel, balance titanium and
30   residual impurities) by including measured amounts of the nickel input material and the

titanium input material in the input electrode for the initial VAR operation. In various embodiments, the accuracy of the initial near-equiatomic nickel-titanium alloy composition may be evaluated by measuring a transition temperature of the VAR ingot, such as, for example, by measuring at least one of the A_s, A_f, M_s, M_f, and M_d of the

5   alloy.

[0052]   It has been observed that the transition temperatures of nickel-titanium alloys depend in large part on the chemical composition of the alloy. In particular, it has been observed that the amount of nickel in solution in the NiTi phase of a nickel-titanium alloy will strongly influence the transformation temperatures of the

10   alloy. For example, the M_s of a nickel-titanium alloy will generally decrease with increasing concentration of nickel in solid solution in the NiTi phase; whereas the M_s of a nickel-titanium alloy will generally increase with decreasing concentration of nickel in solid solution in the NiTi phase. The transformation temperatures of nickel-titanium alloys are well characterized for given alloy compositions. As such, measurement of a

15   transformation temperature, and comparison of the measured value to an expected value corresponding to the target chemical composition of the alloy, may be used to determine any deviation from the target chemical composition of the alloy.

[0053]   Transformation temperatures of a VAR ingot or other intermediate or final mill product may be measured, for example, using differential scanning

20   calorimetry (DSC) or an equivalent thermomechanical test method. In various embodiments, a transformation temperature of a near-equiatomic nickel-titanium alloy VAR ingot may be measured according to ASTM F2004 – 05: *Standard Test Method for Transformation Temperature of Nickel-Titanium Alloys by Thermal Analysis*, which is incorporated by reference into this specification. Transformation temperatures of a VAR

25   ingot or other intermediate or final mill product may also be measured, for example, using bend free recovery (BFR) testing according to ASTM F2082 – 06: *Standard Test Method for Determination of Transformation Temperature of Nickel-Titanium Shape Memory Alloys by Bend and Free Recovery*, which is incorporated by reference into this specification.

[0054]   When a measured transformation temperature deviates from a predetermined specification for the expected transformation temperature of the target alloy composition, the initial VAR ingot may be re-melted in a second VAR operation with a corrective addition of a nickel input material, a titanium input material, or a nickel-

5   titanium master alloy having a known transition temperature. A transformation temperature of the resulting second nickel-titanium alloy VAR ingot may be measured to determine whether the transformation temperature falls within the predetermined specification for the expected transformation temperature of the target alloy composition. The predetermined specification may be a temperature range about the

10   expected transition temperature of the target composition.

[0055]   If a measured transition temperature of a second nickel-titanium VAR ingot falls outside the predetermined specification, the second VAR ingot, and, if necessary, subsequent VAR ingots, may be re-melted in successive VAR operations with corrective alloying additions until a measured transformation temperature falls

15   within the predetermined specification. This iterative re-melting and alloying practice allows for accurate and precise control over the near-equiatomic nickel-titanium alloy composition and transformation temperature. In various embodiments, the A_f, A_s, and/or A_p is/are used to iteratively re-melt and alloy a near-equiatomic nickel-titanium alloy (the austenite peak temperature (A_p) is the temperature at which a nickel-titanium

20   shape-memory or superelastic alloy exhibits the highest rate of transformation from martensite to austenite, see ASTM F2005 – 05: *Standard Terminology for Nickel-Titanium Shape Memory Alloys*, incorporated by reference into this specification).

[0056]   In various embodiments, a titanium input material and a nickel input material may be vacuum induction melted to produce a nickel-titanium alloy, and an

25   ingot of the nickel-titanium alloy may be cast from the VIM melt. The VIM cast ingot may be hot worked and/or cold worked and hot isostatic pressed in accordance with the embodiments described in this specification. The nickel input material may comprise electrolytic nickel or nickel powder, for example, and the titanium input material may be selected from the group consisting of titanium sponge, electrolytic titanium crystals,

30   titanium powders, and iodide-reduced titanium crystal bar. The nickel input material and

the titanium input material may be charged to a VIM crucible, melted together, and cast into an initial VIM ingot.

[0057]   The initial near-equiatomic nickel-titanium alloy composition may be melted as accurately as possible to a predetermined composition (such as, for example,
5   50.8 atomic percent (approximately 55.8 weight percent) nickel, titanium, and residual impurities) by including measured amounts of the nickel input material and the titanium input material in the charge to the VIM crucible. In various embodiments, the accuracy of the initial near-equiatomic nickel-titanium alloy composition may be evaluated by measuring a transition temperature of the VIM ingot or other intermediate or final mill
10   product, as described above in connection with the nickel-titanium alloy prepared using VAR. If a measured transition temperature falls outside a predetermined specification, the initial VIM ingot, and, if necessary, subsequent VIM ingots or other intermediate or final mill products, may be re-melted in successive VIM operations with corrective alloying additions until a measured transformation temperature falls within the
15   predetermined specification.

[0058]   In various embodiments, a nickel-titanium alloy may be produced using a combination of one or more VIM operations and one or more VAR operations. For example, a nickel-titanium alloy ingot may be prepared from nickel input materials and titanium input materials using a VIM operation to prepare an initial ingot, which is
20   then remelted in a VAR operation. A bundled VAR operation may also be used in which a plurality of VIM ingots are used to construct a VAR electrode.

[0059]   In various embodiments, a nickel-titanium alloy may comprise 45.0 atomic percent to 55.0 atomic percent nickel, balance titanium and residual impurities. The nickel-titanium alloy may comprise 45.0 atomic percent to 56.0 atomic percent
25   nickel or any sub-range subsumed therein, such as, for example, 49.0 atomic percent to 52.0 atomic percent nickel. The nickel-titanium alloy may also comprise 50.8 atomic percent nickel ($\pm$ 0.5, $\pm$0.4, $\pm$0.3, $\pm$0.2, or $\pm$0.1 atomic percent nickel), balance titanium and residual impurities. The nickel-titanium alloy may also comprise 55.04 atomic percent nickel ($\pm$ 0.10, $\pm$ 0.05, $\pm$0.04, $\pm$0.03, $\pm$0.02, or $\pm$0.01 atomic percent nickel),
30   balance titanium and residual impurities.

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[0060]   In various embodiments, a nickel-titanium alloy may comprise 50.0 weight percent to 60.0 weight percent nickel, balance titanium and residual impurities. The nickel-titanium alloy may comprise 50.0 weight percent to 60.0 weight percent nickel or any sub-range subsumed therein, such as, for example, 54.2 weight percent to

5   57.0 weight percent nickel. The nickel-titanium alloy may comprise 55.8 weight percent nickel (± 0.5, ±0.4, ±0.3, ±0.2, or ± 0.1 weight percent nickel), balance titanium and residual impurities. The nickel-titanium alloy may comprise 54.5 weight percent nickel (± 2, ±1, ± 0.5, ±0.4, ±0.3, ±0.2, or ± 0.1 weight percent nickel), balance titanium and residual impurities.

10   [0061]   The various embodiments described in this specification are also applicable to shape-memory or superelastic nickel-titanium alloys comprising at least one alloying element in addition to nickel and titanium, such as, for example, copper, iron, cobalt, niobium, chromium, hafnium, zirconium, platinum, and/or palladium. In various embodiments, a shape-memory or superelastic nickel-titanium alloy may

15   comprise nickel, titanium, residual impurities, and 1.0 atomic percent to 30.0 atomic percent of at least one other alloying element, such as, for example, copper, iron, cobalt, niobium, chromium, hafnium, zirconium, platinum, and palladium. For example, a shape-memory or superelastic nickel-titanium alloy may comprise nickel, titanium, residual impurities, and 5.0 atomic percent to 30.0 atomic percent hafnium, zirconium,

20   platinum, palladium, or a combination of any thereof. In various embodiments, a shape-memory or superelastic nickel-titanium alloy may comprise nickel, titanium, residual impurities, and 1.0 atomic percent to 5.0 atomic percent copper, iron, cobalt, niobium, chromium, or a combination of any thereof.

[0062]   The non-limiting and non-exhaustive examples that follow are

25   intended to further describe various non-limiting and non-exhaustive embodiments without restricting the scope of the embodiments described in this specification.

EXAMPLES

Example 1:

[0063]   A 0.5-inch diameter nickel-titanium alloy bar was cut into seven (7)
bar samples. The sections were respectively treated as indicated in Table 1.

5   Table 1

Sample Number	Treatment
1	None
2	HIP'ed: 800°C; 15,000 psi; 2 hours
3	HIP'ed: 850°C; 15,000 psi; 2 hours
4	HIP'ed: 900°C; 15,000 psi; 2 hours
5	HIP'ed: 800°C; 45,000 psi; 2 hours
6	HIP'ed: 850°C; 45,000 psi; 2 hours
7	HIP'ed: 900°C; 45,000 psi; 2 hours

[0064]   After the hot isostatic pressing treatment, Samples 2-7 were each
sectioned longitudinally at the approximate centerline of the samples to produce
samples for scanning electron microscopy (SEM). Sample 1 was sectioned
10   longitudinally in the as-received condition without any hot isostatic pressing treatment.
The maximum size and area fraction of contiguous non-metallic inclusions and porosity
voids were measured in accordance with ASTM E1245 – 03 (2008) – *Standard Practice
for Determining the Inclusion or Second-Phase Constituent Content of Metals by
Automatic Image Analysis.* The full longitudinal cross-sections were inspected using
15   SEM in backscatter electron mode. SEM fields containing the three largest visible
regions of contiguous non-metallic inclusions and porosity were imaged at 500x
magnification for each sectioned sample. Image analysis software was used to
measure the maximum size and the area fraction of the non-metallic inclusions and
porosity in each of the three SEM images per sectioned sample. The results are
20   presented in Tables 2 and 3.

Table 2

Sample Number	Maximum Inclusion Dimension (micrometers)	Maximum Area Fraction (%)	SEM Image Corresponding to Maximum Inclusion Dimension
1	51.5	1.88	Figure 4A
2	43.6	2.06	Figure 4B
3	35.9	1.44	Figure 4C
4	29.4	1.46	Figure 4D
5	32.1	1.87	Figure 4E
6	29.4	1.86	Figure 4F
7	38.8	1.84	Figure 4G

Table 3

Sample Number	Average of the Three Maximum Inclusion Dimensions (micrometers)	Average of the Three Maximum Area Fractions (%)
1	49.1	1.57
2	39.3	1.73
3	33.8	1.28
4	27.7	1.18
5	30.1	1.42
6	28.8	1.49
7	34.8	1.55

[0065] The results show that the hot isostatic pressing operations generally decreased the combined sizes and area fractions of the non-metallic inclusions and porosity. The hot isostatic pressed nickel-titanium alloy bars generally met the requirements of the ASTM F 2063 – 12 standard specification (maximum allowable length dimension of 39.0 micrometers (0.0015 inch), and maximum area fraction of 2.8%). A comparison of Figures 4B-4G with Figure 4A shows that the hot isostatic pressing operations decreased and in some cases eliminated porosity in the nickel-titanium alloy bars.

Example 2:

[0066]   A 0.5-inch diameter nickel-titanium alloy bar was cut into seven (7) bar samples. The samples were respectively treated as indicated in Table 4.

Table 4

Sample Number	Treatment
1	None
2	HIP'ed: 800°C; 15,000 psi; 2 hours
3	HIP'ed: 850°C; 15,000 psi; 2 hours
4	HIP'ed: 900°C; 15,000 psi; 2 hours
5	HIP'ed: 800°C; 45,000 psi; 2 hours
6	HIP'ed: 850°C; 45,000 psi; 2 hours
7	HIP'ed: 900°C; 45,000 psi; 2 hours

5

[0067]   After the hot isostatic pressing treatment, Samples 2-7 were each sectioned longitudinally at the approximate centerline of the samples to produce sections for scanning electron microscopy (SEM). Samples 1 was sectioned longitudinally in the as-received condition without any hot isostatic pressing treatment.

10   The maximum size and area fraction of contiguous non-metallic inclusions and porosity voids were measured in accordance with ASTM E1245 – 03 (2008) – *Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals by Automatic Image Analysis*. The full longitudinal cross-sections were inspected using SEM in backscatter electron mode. SEM fields containing the three largest visible

15   regions of contiguous non-metallic inclusions and porosity were imaged at 500x magnification for each sectioned sample. Image analysis software was used to measure the maximum size and the area fraction of the non-metallic inclusions and porosity in each of the three SEM images per sectioned sample. The results are presented in Tables 5 and 6.

20

Table 5

Sample Number	Maximum Inclusion Dimension (micrometers)	Maximum Area Fraction (%)	SEM Image Corresponding to Maximum Inclusion Dimension
1	52.9	1.63	Figure 5A
2	41.7	1.23	Figure 5B
3	28.3	1.63	Figure 5C
4	29.9	0.85	Figure 5D
5	34.1	0.95	Figure 5E
6	30.2	1.12	Figure 5F
7	34.7	1.25	Figure 5G

Table 6

Section Number	Average of Three Maximum Inclusion Dimensions (micrometers)	Average of Three Maximum Area Fractions (%)
1	49.0	1.45
2	37.0	1.15
3	27.8	1.28
4	27.9	0.80
5	32.8	0.88
6	29.0	1.05
7	33.1	1.11

[0068]   The results show that the hot isostatic pressing operations generally decreased the combined sizes and area fractions of the non-metallic inclusions and porosity. The hot isostatic pressed nickel-titanium alloy bars generally met the requirements of the ASTM F 2063 – 12 standard specification (maximum allowable length dimension of 39.0 micrometers (0.0015 inch), and maximum area fraction of 2.8%). A comparison of Figures 5B-5G with Figure 5A shows that the hot isostatic pressing operations decreased and in some cases eliminated porosity in the nickel-titanium alloy bars.

Example 3:

[0069]   A 0.5-inch diameter nickel-titanium alloy bar was hot isostatic

pressed for 2 hours at 900°C and 15,000 psi. The hot isostatic pressed bar was

sectioned longitudinally to produce eight (8) longitudinal sample sections for scanning

5   electron microscopy (SEM). The maximum size and area fraction of contiguous non-

metallic inclusions and porosity voids were measured in accordance with ASTM E1245

– 03 (2008) – *Standard Practice for Determining the Inclusion or Second-Phase*

Constituent Content of Metals by Automatic Image Analysis. Each of the eight

longitudinal cross-sections was inspected using SEM in backscatter electron mode.

10   SEM fields containing the three largest visible regions of contiguous non-metallic

inclusions and porosity were imaged at 500x magnification for each sample section.

Image analysis software was used to measure the maximum size and the area fraction

of the non-metallic inclusions and porosity in each of the three SEM images per sample

section. The results are presented in Table 7.

15   Table 7

Sample Section	Maximum Inclusion Dimension (micrometers)	Maximum Area Fraction (%)	SEM Image Corresponding to Maximum Inclusion Dimension
1	34.7	1.15	Figure 6A
2	29.0	1.09	Figure 6B
3	28.7	1.23	Figure 6C
4	34.7	1.20	Figure 6D
5	32.8	1.42	Figure 6E
6	28.3	1.23	Figure 6F
7	35.4	0.95	Figure 6G
8	34.4	1.03	Figure 6H
Average	32.3	1.20	---

[0070]   The results show that the hot isostatic pressed nickel-titanium alloy

bars generally met the requirements of the ASTM F 2063 – 12 standard specification

(maximum allowable length dimension of 39.0 micrometers (0.0015 inch), and

maximum area fraction of 2.8%). A study of Figures 6A-6H shows that the hot isostatic pressing operations eliminated porosity in the nickel-titanium alloy bars.

Example 4:

5   [0071]   Two (2) 4.0-inch diameter nickel-titanium alloy billets (Billet-A and Billet-B) were each cut into two (2) smaller billets to produce a total of four (4) billet samples: A1, A2, B1, and B2. The sections were respectively treated as indicated in Table 8.

Table 8

Billet Samples	Treatment (Billet-A)
A1	None
A2	HIP'ed: 900°C; 15 ksi; 2 hours
B1	None
B2	HIP'ed: 900°C; 15 ksi; 2 hours

10

        [0072]   After the hot isostatic pressing treatment, Samples A2 and B2 were each sectioned longitudinally at the approximate centerline of the sections to produce samples for scanning electron microscopy (SEM). Samples A1 and B1 were sectioned longitudinally in the as-received condition without any hot isostatic pressing treatment.

15   The maximum size and area fraction of contiguous non-metallic inclusions and porosity voids were measured in accordance with ASTM E1245 – 03 (2008) – *Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals by Automatic Image Analysis*. The full longitudinal cross-sections were inspected using SEM in backscatter electron mode. SEM fields containing the three largest visible

20   regions of contiguous non-metallic inclusions and porosity were imaged at 500x magnification for each sectioned sample. Image analysis software was used to measure the maximum size and the area fraction of the non-metallic inclusions and porosity in each of the three SEM images per sectioned sample. The results are presented in Table 9.

Table 9

Sample	Maximum Inclusion Dimension (micrometers)	Maximum Area Fraction (%)	SEM Image Corresponding to Maximum Inclusion Dimension
A1	68.7	1.66	Figure 7A
A2	48.5	1.85	Figure 7B
B1	69.9	1.56	Figure 7C
B2	45.2	1.59	Figure 7D

[0073]   The results show that the hot isostatic pressing operations generally decreased the combined sizes and area fractions of the non-metallic inclusions and porosity. A comparison of Figures 7A and 7C with Figures 7B and 7D, respectively, shows that the hot isostatic pressing operations decreased and in some cases eliminated porosity in the nickel-titanium alloy billets.

Example 5:

[0074]   A nickel-titanium alloy ingot was hot forged, hot rolled, and cold drawn to produce a 0.53-inch diameter bar. The nickel-titanium alloy bar was hot isostatic pressed for 2 hours at 900°C and 15,000 psi. The hot isostatic pressed bar was sectioned longitudinally to produce five (5) longitudinal sample sections for scanning electron microscopy (SEM). The maximum size and area fraction of contiguous non-metallic inclusions and porosity voids were measured in accordance with ASTM E1245 – 03 (2008) – Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals by Automatic Image Analysis. Each of the five longitudinal cross-sections was inspected using SEM in backscatter electron mode. SEM fields containing the three largest visible regions of contiguous non-metallic inclusions and porosity were imaged at 500x magnification for each sample section. Image analysis software was used to measure the maximum size and the area fraction

of the non-metallic inclusions and porosity in each of the three SEM images per sample
section. The results are presented in Table 10.

Table 10

Sample Section	Maximum Inclusion Dimension (micrometers)	Maximum Area Fraction (%)	SEM Image Corresponding to Maximum Inclusion
1	36.8	1.78	Figure 8A
2	34.3	1.36	Figure 8B
3	37.1	1.21	Figure 8C
4	37.7	1.60	Figure 8D
5	45.0	1.69	Figure 8E
Average	38.2	1.53	---

5   [0075]   The results show that the cold drawn and hot isostatic pressed
nickel-titanium alloy bar generally met the requirements of the ASTM F 2063 – 12
standard specification (maximum allowable length dimension of 39.0 micrometers
(0.0015 inch), and maximum area fraction of 2.8%). A study of Figures 6A-6H shows
that the hot isostatic pressing operations eliminated porosity in the nickel-titanium alloy
10   bars.

       [0076]   This specification has been written with reference to various non-
limiting and non-exhaustive embodiments. However, it will be recognized by persons
having ordinary skill in the art that various substitutions, modifications, or combinations
of any of the disclosed embodiments (or portions thereof) may be made within the
15   scope of this specification. Thus, it is contemplated and understood that this
specification supports additional embodiments not expressly set forth herein. Such
embodiments may be obtained, for example, by combining, modifying, or reorganizing
any of the disclosed steps, components, elements, features, aspects, characteristics,
limitations, and the like, of the various non-limiting and non-exhaustive embodiments
20   described in this specification. In this manner, Applicant reserves the right to amend the
claims during prosecution to add features as variously described in this specification,

and such amendments comply with the requirements of 35 U.S.C. §§ 112(a) and 132(a).

CLAIMS

What is claimed is:

5 1.   A process for the production of a nickel-titanium mill product comprising:
         hot forging a nickel-titanium alloy ingot at a temperature greater than or equal to
   500°C to produce a nickel-titanium alloy billet;
         hot bar rolling the nickel-titanium alloy billet at a temperature greater than or
   equal to 500°C to produce a nickel-titanium alloy workpiece;
10   cold drawing the nickel-titanium alloy workpiece at a temperature less than
   500°C to produce a nickel-titanium alloy bar; and
         hot isostatic pressing the cold worked nickel-titanium alloy bar for at least 0.25
   hour in a HIP furnace operating at a temperature in the range of 700°C to 1000°C and a
   pressure in the range of 3,000 psi to 50,000 psi.
15

   2.   The process of claim 1, wherein the nickel-titanium alloy workpiece is hot isostatic
   pressed (HIP) for at least 1.0 hour in a HIP furnace operating at a temperature in the
   range of 800°C to 950°C and a pressure in the range of 10,000 psi to 17,000 psi.

20 3.   The process of claim 1, wherein the hot forging and the hot bar rolling are
   independently performed at an initial workpiece temperature in the range of 600°C to
   900°C.

   4.   The process of claim 1, wherein the nickel-titanium alloy workpiece is cold drawn
25 at ambient temperature.

   5.   The process of claim 1, wherein the process produces a bar mill product that
   meets size and area fraction requirements of ASTM F 2063 – 12.

30

6.   A process for the production of a nickel-titanium mill product comprising:

hot working a nickel-titanium alloy workpiece at a temperature of greater than or equal to 500°C;

cold working the hot worked nickel-titanium alloy workpiece at a temperature less
5   than 500°C; and

hot isostatic pressing the cold worked nickel-titanium alloy workpiece for at least 0.25 hour in a HIP furnace operating at a temperature in the range of 700°C to 1000°C and a pressure in the range of 3,000 psi to 50,000 psi.

10   7.   The process of claim 6, wherein the nickel-titanium alloy workpiece is hot isostatic pressed (HIP) for at least 1.0 hour in a HIP furnace operating at a temperature in the range of 800°C to 950°C and a pressure in the range of 10,000 psi to 17,000 psi.

8.   The process of claim 6, wherein the hot working is performed at an initial
15   workpiece temperature in the range of 600°C to 900°C.

9.   The process of claim 6, wherein the nickel-titanium alloy workpiece is cold worked at ambient temperature.

20   10.   The process of claim 6, wherein the process produces a bar mill product that meets size and area fraction requirements of ASTM F 2063 – 12.

11.   A process for the production of a nickel-titanium mill product comprising:

cold working a nickel-titanium alloy workpiece at a temperature less than 500°C;
25   and

hot isostatic pressing the cold worked nickel-titanium alloy workpiece.

12.   The process of claim 11, wherein the nickel-titanium alloy workpiece is cold worked at a temperature less than 100°C.
30

13.   The process of claim 11, wherein the nickel-titanium alloy workpiece is cold worked at ambient temperature.

14.   The process of claim 11, wherein the cold working comprises at least one cold

5   working technique selected from the group consisting of forging, upsetting, drawing, rolling, extruding, pilgering, rocking, swaging, heading, coining, and combinations of any thereof.

15.   The process of claim 11, comprising:

10   cold working the nickel-titanium alloy workpiece in a first cold working operation at ambient temperature;

        annealing the cold worked nickel-titanium alloy workpiece;

        cold working the nickel-titanium alloy workpiece in a second cold working operation at ambient temperature; and

15   hot isostatic pressing the twice cold worked nickel-titanium alloy workpiece.

16.   The process of claim 15, further comprising, after the second cold working operation and before the hot isostatic pressing, subjecting the nickel-titanium alloy workpiece to:

20   at least one additional intermediate annealing operation; and

        at least one additional cold working operation at ambient temperature.

17.   The process of claim 15, wherein the nickel-titanium alloy workpiece is annealed at a temperature in the range of 700°C to 900°C.

25

18.   The process of claim 15, wherein the nickel-titanium alloy workpiece is annealed for at least 20 seconds furnace time.

30

19.   The process of claim 11, wherein the nickel-titanium alloy workpiece is hot isostatic pressed (HIP) for at least 0.25 hour in a HIP furnace operating at a temperature in the range of 700°C to 1000°C and a pressure in the range of 3,000 psi to 50,000 psi

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20.   The process of claim 11, wherein the nickel-titanium alloy workpiece is hot isostatic pressed (HIP) in a HIP furnace operating at a temperature in the range of 800°C to 1000°C and a pressure in the range of 7,500 psi to 20,000 psi.

10   21.   The process of claim 11, wherein the nickel-titanium alloy workpiece is hot isostatic pressed (HIP) in a HIP furnace operating at a temperature in the range of 800°C to 950°C and a pressure in the range of 10,000 psi to 17,000 psi.

22.   The process of claim 11, wherein the nickel-titanium alloy workpiece is hot
15   isostatic pressed (HIP) in a HIP furnace operating at a temperature in the range of 850°C to 900°C and a pressure in the range of 12,000 psi to 15,000 psi.

23.   The process of claim 11, wherein the nickel-titanium alloy workpiece is hot isostatic pressed (HIP) for at least 2.0 hours in a HIP furnace operating at a temperature
20   in the range of 800°C to 1000°C and a pressure in the range of 7,500 psi to 20,000 psi.

24.   The process of claim 11, further comprising hot working the nickel-titanium alloy workpiece before the cold working.

25   25.   The process of claim 24, wherein the hot working is performed at an initial workpiece temperature in the range of 600°C to 900°C.

26.   The process of claim 11, wherein the process produces a mill product selected from the group consisting of a billet, a bar, a rod, a wire, a tube, a slab, a plate, and a
30   sheet.

27. The process of claim 11, wherein:

the cold working reduces size and area fraction of non-metallic inclusions in the nickel-titanium alloy workpiece; and

the hot isostatic pressing reduces porosity in the nickel-titanium alloy workpiece.

5

28. The process of claim 1, wherein the process produces a mill product that meets the size and area fraction requirements of ASTM F 2063 – 12.

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FIG. 1

FIG. 2A

FIG. 2B

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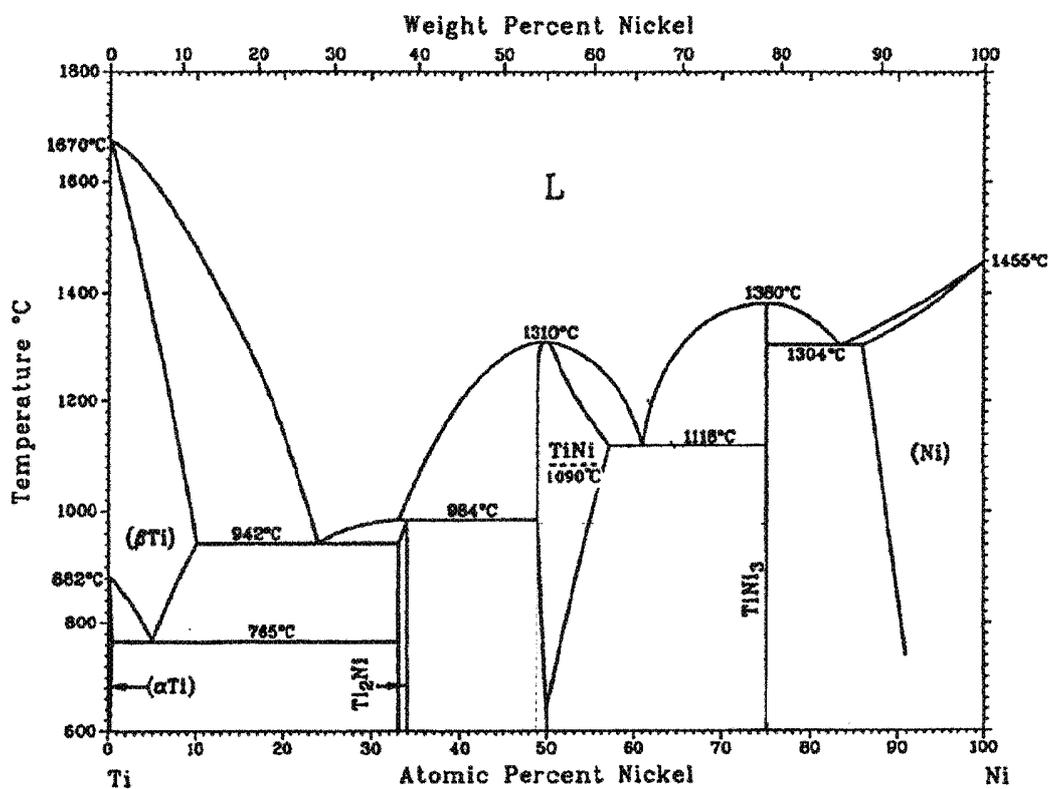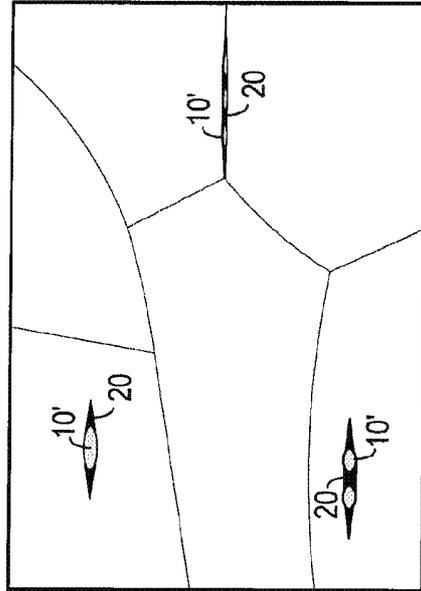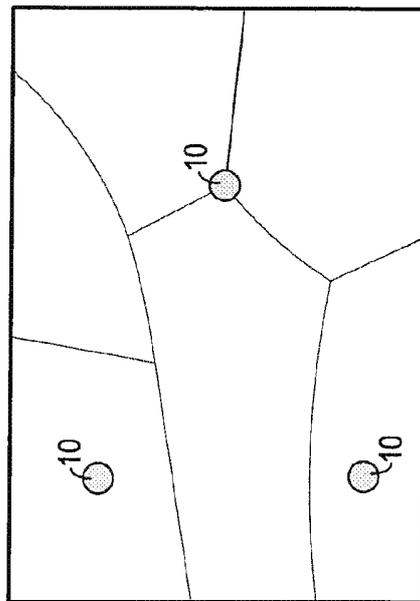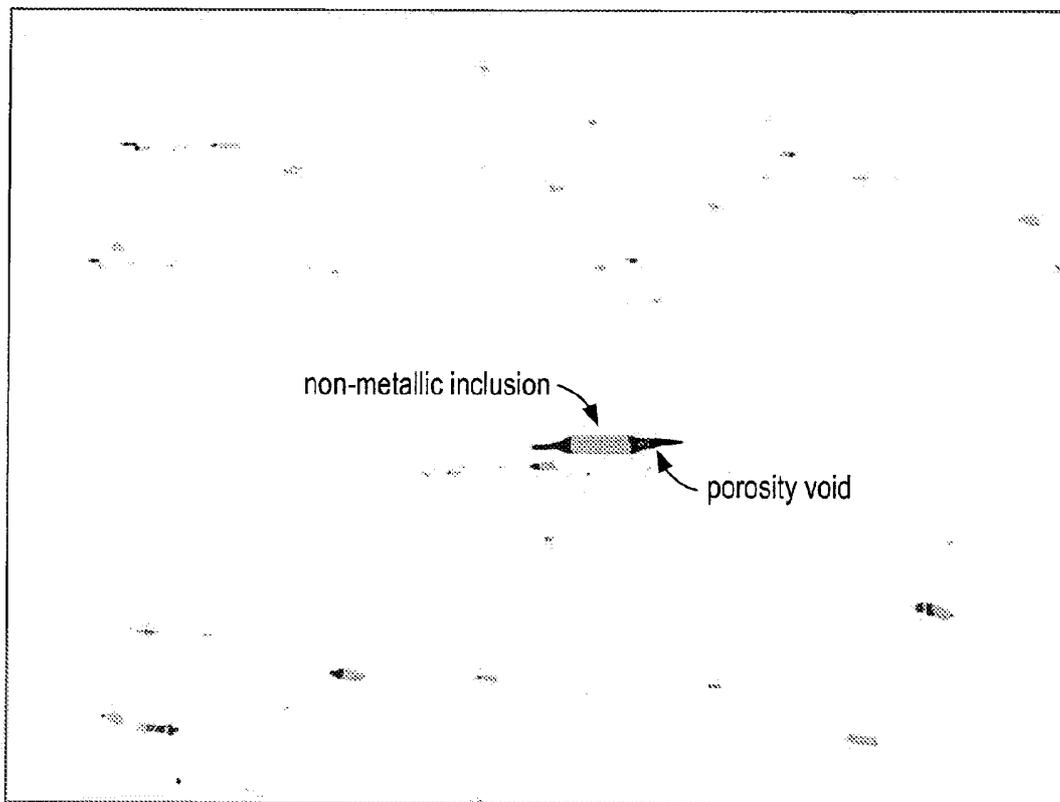
FIG. 3

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FIG. 4A

FIG. 4B

FIG. 4C
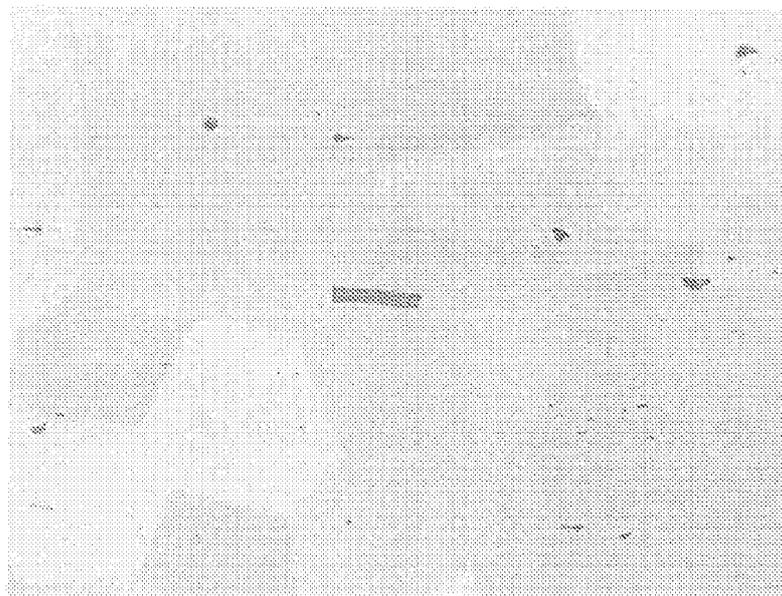
FIG. 4D

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FIG. 4E

FIG. 4F

FIG. 4G

FIG. 5A
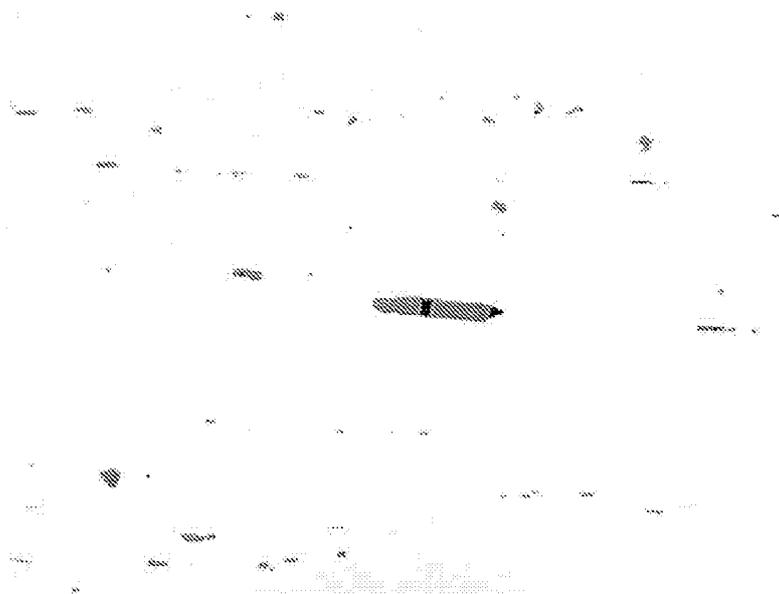
FIG. 5B

FIG. 5C

FIG. 5D
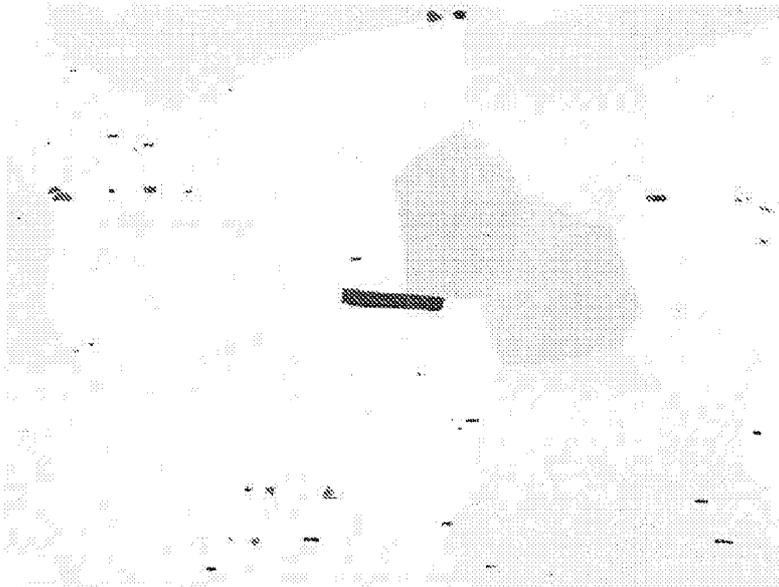
FIG. 5E
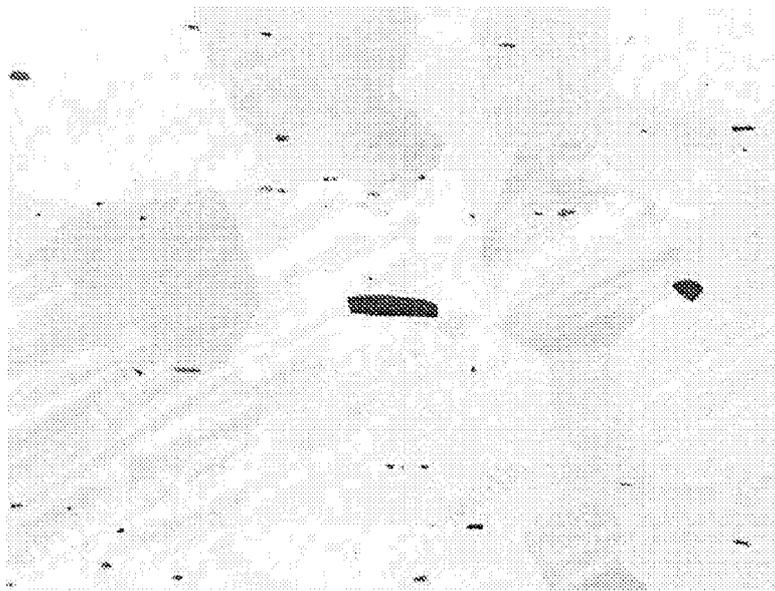
FIG. 5F

FIG. 5G

12/20
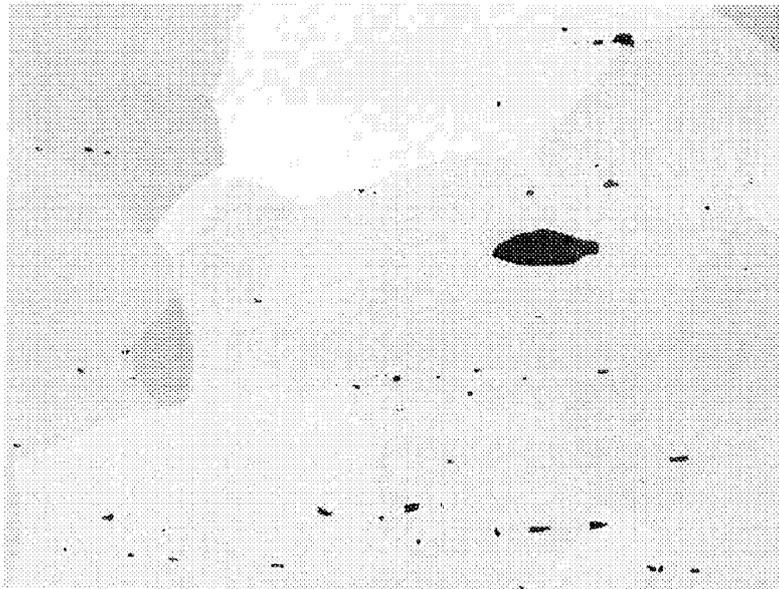
FIG. 6A

FIG. 6B

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FIG. 6C
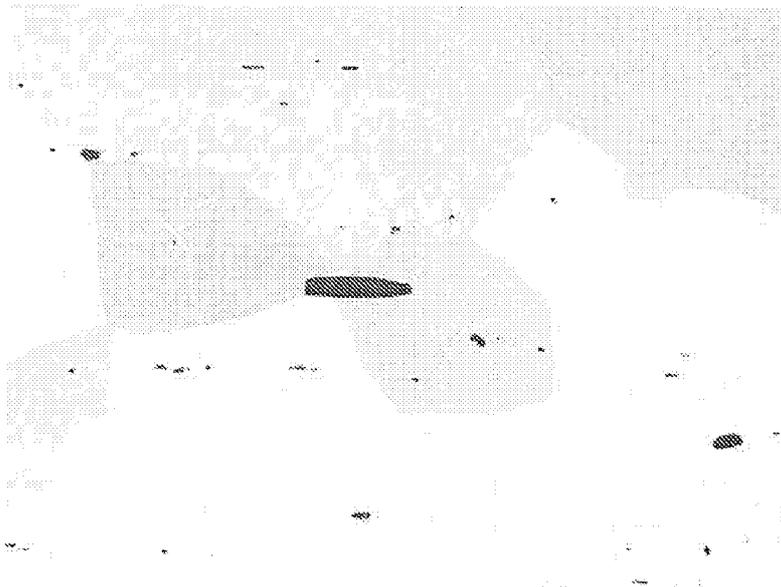
FIG. 6D
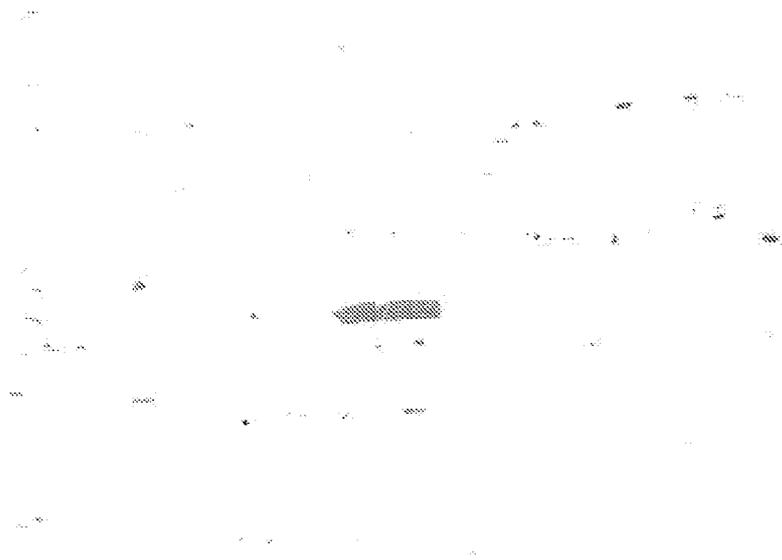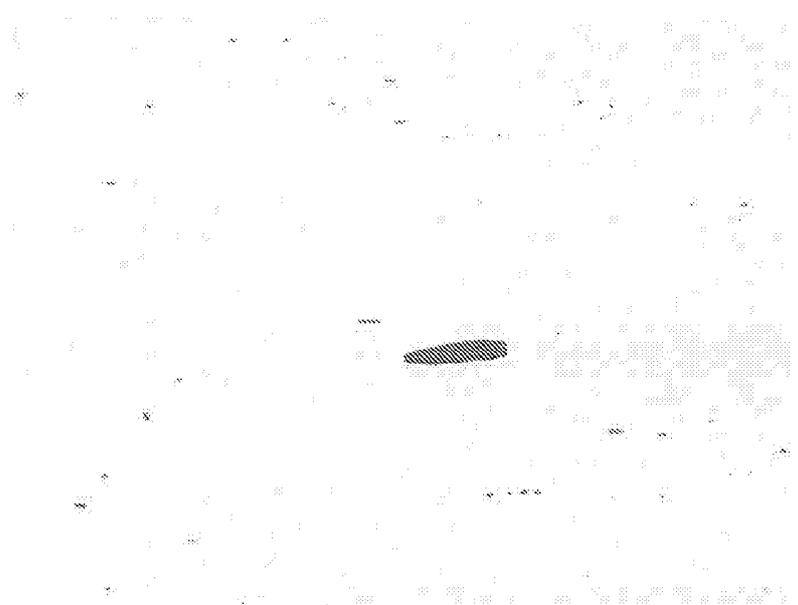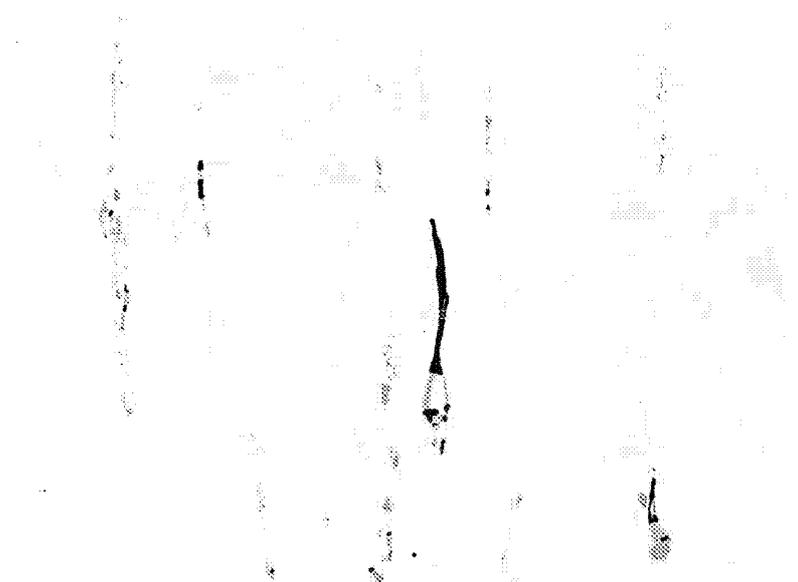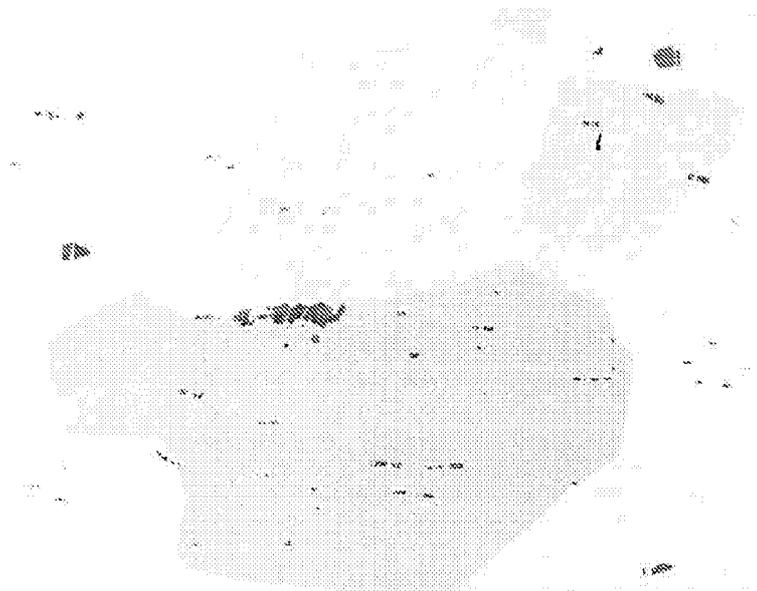
FIG. 6E

FIG. 6F

FIG. 6G

FIG. 6H

FIG. 7A

FIG. 7B

FIG. 7C

FIG. 7D

FIG. 8A

FIG. 8B

FIG. 8C

FIG. 8D

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FIG. 8E

(54) Title: THERMO-MECHANICAL PROCESSING OF NICKEL-TITANIUM ALLOYS

(57) Abstract: Processes for the production of nickel-titanium mill products are disclosed. A nickel-titanium alloy workpiece is cold worked at a temperature less than 500 C. The cold worked nickel-titanium alloy workpiece is hot isostatic pressed (HIP'ed).

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C22F1/00   C22C14/00   C22C19/00
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22F C22C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	SCOTT M RUSSELL: "Nitinol Melting and Fabrication", SMST. CONFERENCE PROCEEDINGS, INTERNATIONAL ORGANIZATION OF SHAPE MEMORY AND SUPERELASTIC TECHNOLOGY, XX, XX, 1 January 2000 (2000-01-01), pages 1-9, XP002456650, page 2 - page 8 -----	1-28
A	WO 01/12359 A1 (NITINOL TECHNOLOGIES INC [US]; JULIEN GERALD J [US]) 22 February 2001 (2001-02-22) page 8, line 6 - page 9, line 6 -----	1-28
A	JP 2009 013461 A (NEC TOKIN CORP) 22 January 2009 (2009-01-22) paragraph [0021] -----	1-28
	-/--	

[X] Further documents are listed in the continuation of Box C.   [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
6 November 2014	25/11/2014

| Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016 | Authorized officer Liu, Yonghe |

Form PCT/ISA/210 (second sheet) (April 2005)

1

C(Continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2012/039740 A1 (WOJCIK C CRAIG [US]) 16 February 2012 (2012-02-16) claims 1-30 -----	1-28
A	WO 02/058866 A2 (SCIMED LIFE SYSTEMS INC [US]) 1 August 2002 (2002-08-01) claims 1-43 -----	1-28

1

Form PCT/ISA/210 (continuation of second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

Information on patent family members

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 0112359	A1	22-02-2001	AU	6786800 A	13-03-2001
			CA	2381785 A1	22-02-2001
			EP	1224045 A1	24-07-2002
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			US	2002098105 A1	25-07-2002
			WO	02058866 A2	01-08-2002

(54) 发明名称
镍-钛合金的热机械处理

(57) 摘要
本申请公开了用于生产镍-钛轧制产品的方法。镍-钛合金工件在低于500℃温度下被冷加工。冷加工的镍-钛合金工件被热等静压压制(HIP'ed)。

CN 104662185 A

1. 一种用于生产镍－钛轧制产品的方法,其包括:

在大于或等于 500℃的温度下热锻造镍－钛合金锭以产生镍－钛合金坯料;

在大于或等于 500℃的温度下热棒轧所述镍－钛合金坯料以产生镍－钛合金工件;

在低于 500℃的温度下将所述镍－钛合金工件冷拉拔以产生镍－钛合金棒;和

在于 700℃至 1000℃范围内的温度和 3,000psi 至 50,000psi 范围内的压力下操作的 HIP 炉中,将所述冷加工的镍－钛合金棒热等静压压制至少 0.25 小时。

2. 根据权利要求 1 所述的方法,其中在于 800℃至 950℃范围内的温度和 10,000psi 至 17,000psi 范围内的压力下操作的 HIP 炉中,将所述镍－钛合金工件热等静压压制 (HIP) 至少 1.0 小时。

3. 根据权利要求 1 所述的方法,其中在于 600℃至 900℃范围内的初始工件温度下独立地实施所述热锻造和所述热棒轧。

4. 根据权利要求 1 所述的方法,其中在环境温度下冷拉拔所述镍－钛合金工件。

5. 根据权利要求 1 所述的方法,其中所述方法生产出满足 ASTM F 2063-12 的尺寸和面积分率要求的棒轧制产品。

6. 一种用于生产镍－钛轧制产品的方法,其包括:

在大于或等于 500℃的温度下热加工镍－钛合金工件;

在低于 500℃的温度下冷加工所述热加工的镍－钛合金工件;和

在于 700℃至 1000℃范围内的温度和 3,000psi 至 50,000psi 范围内的压力下操作的 HIP 炉中,将所述冷加工的镍－钛合金工件热等静压压制至少 0.25 小时。

7. 根据权利要求 6 所述的方法,其中在于 800℃至 950℃范围内的温度和 10,000psi 至 17,000psi 范围内的压力下操作的 HIP 炉中,将所述镍－钛合金工件热等静压压制 (HIP) 至少 1.0 小时。

8. 根据权利要求 6 所述的方法,其中在于 600℃至 900℃范围内的初始工件温度下独立地实施所述热加工。

9. 根据权利要求 6 所述的方法,其中在环境温度下冷加工所述镍－钛合金工件。

10. 根据权利要求 6 所述的方法,其中所述方法生产出满足 ASTM F 2063-12 的尺寸和面积分率要求的棒轧制产品。

11. 一种用于生产镍－钛轧制产品的方法,其包括:

在低于 500℃的温度下冷加工镍－钛合金工件;和

热等静压压制所述冷加工的镍－钛合金工件。

12. 根据权利要求 11 所述的方法,其中在低于 100℃的温度下冷加工所述镍－钛合金工件。

13. 根据权利要求 11 所述的方法,其中在环境温度下冷加工所述镍－钛合金工件。

14. 根据权利要求 11 所述的方法,其中所述冷加工包括至少一种选自由锻造、镦粗、拉拔、轧制、挤出、皮尔格式轧制、摆辗、型锻、顶锻、压印和它们的任意组合组成的组的冷加工技术。

15. 根据权利要求 11 所述的方法,其包括:

在第一冷加工操作中,在环境温度下冷加工所述镍－钛合金工件;

将所述冷加工的镍－钛合金工件退火;

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在第二冷加工操作中，在环境温度下冷加工所述镍－钛合金工件；和

热等静压压制两次冷加工的镍－钛合金工件。

16. 根据权利要求 15 所述的方法，其进一步包括，在所述第二冷加工操作之后和所述热等静压压制之前，使所述镍－钛合金工件经受：

至少一个额外的中间退火操作；和

至少一个额外的在环境温度下的冷加工操作。

17. 根据权利要求 15 所述的方法，其中在于 700℃ 至 900℃ 范围内的温度下将所述镍－钛合金工件退火。

18. 根据权利要求 15 所述的方法，其中将所述镍－钛合金工件退火至少 20 秒炉时间。

19. 根据权利要求 11 所述的方法，其中在于 700℃ 至 1000℃ 范围内的温度和 3,000psi 至 50,000psi 范围内的压力下操作的 HIP 炉中，将所述镍－钛合金工件热等静压压制 (HIP) 至少 0.25 小时。

20. 根据权利要求 11 所述的方法，其中在于 800℃ 至 1000℃ 范围内的温度和 7,500psi 至 20,000psi 范围内的压力下操作的 HIP 炉中，将所述镍－钛合金工件热等静压压制 (HIP)。

21. 根据权利要求 11 所述的方法，其中在于 800℃ 至 950℃ 范围内的温度和 10,000psi 至 17,000psi 范围内的压力下操作的 HIP 炉中，将所述镍－钛合金工件热等静压压制 (HIP)。

22. 根据权利要求 11 所述的方法，其中在于 850℃ 至 900℃ 范围内的温度和 12,000psi 至 15,000psi 范围内的压力下操作的 HIP 炉中，将所述镍－钛合金工件热等静压压制 (HIP)。

23. 根据权利要求 11 所述的方法，其中在于 800℃ 至 1000℃ 范围内的温度和 7,500psi 至 20,000psi 范围内的压力下操作的 HIP 炉中，将所述镍－钛合金工件热等静压压制 (HIP) 至少 2.0 小时。

24. 根据权利要求 11 所述的方法，其进一步包括在所述冷加工之前热加工所述镍－钛合金工件。

25. 根据权利要求 24 的方法，其中在于 600℃ 至 900℃ 的范围内的初始工件温度下实施所述热加工。

26. 根据权利要求 11 所述的方法，其中所述方法生产出选自由坯料、棒、杆、线、管、厚板、板和片材组成的组的轧制产品。

27. 根据权利要求 11 所述的方法，其中：

所述冷加工降低了所述镍－钛合金工件中的非金属夹杂物的尺寸和面积分率；和

所述热等静压压制减少了所述镍－钛合金工件中的孔隙。

28. 根据权利要求 1 所述的方法，其中所述方法生产出满足 ASTM F 2063-12 的尺寸和面积分率要求的轧制产品。

镍-钛合金的热机械处理

技术领域

[0001]　本说明书中涉及用于生产镍-钛合金轧制产品的方法以及通过本说明书中所描述的方法制得的轧制产品。

[0002]　发明背景

[0003]　等原子的和近等原子的镍-钛合金具有"形状记忆"和"超弹性"二者的属性。更具体地,已知当通常被称为"镍钛诺(Nitinol)"合金的这些合金冷却至低于该合金的马氏体开始温度(martensite start temperature)("M_s")时,这些合金经历从母相(通常称为奥氏体相(austenite phase))到至少一个马氏体相(martensite phase)的马氏体相变(martensitic transformation)。当冷却至该合金的马氏体结束温度(martensite finish temperature)("M_f")时完成该相变。此外,当材料被加热到高于其奥氏体结束温度(austenite finish temperature)("A_f")的温度时,该相变是可逆的。

[0004]　这种可逆的马氏体相变产生了合金的形状记忆属性。例如,镍-钛形状记忆合金可被制成仍在奥氏体相中的第一形状(即,在高于合金的A_f的温度),随后被冷却至低于M_f的温度并变形为第二形状。只要材料保持低于该合金的奥氏体开始温度(austenite start temperature)("A_s")(即,开始转变成奥氏体时的温度),该合金将保持所述第二形状。然而,如果形状记忆合金被加热到高于A_f的温度,则该合金将恢复到所述第一形状,如果没有被物理约束或当被约束可以施加应力至另一制品上时。镍-钛合金通常可实现高至8%的可回收应变,原因在于可逆的奥氏体至马氏体热诱导转变(thermally-induced transition),并因此称为术语"形状记忆"。

[0005]　在奥氏体相和马氏体相之间的相变还产生了形状记忆镍-钛合金的"拟弹性"或"超弹性"属性。当形状记忆镍-钛合金在高于该合金的A_f温度但在低于所谓的马氏体变形温度(martensite deformation temperature)("M_d")的温度下产生应变时,该合金可经历从奥氏体相到马氏体相的应力诱导相变。因此所述M_d被定义成大于该马氏体不能被应力诱导时的温度的温度。当在A_f和M_d之间的温度下将应力施加于镍-钛合金时,在小的弹性变形之后,该合金通过从奥氏体至马氏体的相变而屈服于所施加的应力。这种相变,结合马氏体相在所施加的应力下通过由孪晶界(twinned boundary)的移动变形而不产生位错(dislocation)的能力,允许镍-钛合金通过无塑性(即永久)变形的弹性变形来吸收大量的应变能。当应变被去除时,该合金能够恢复回到其非应变的状态,并因此称为术语"拟弹性"。镍-钛合金通常可实现高至8%的可回收应变,原因在于可逆的奥氏体至马氏体应力诱导转变(stress-induced transition),并因此称为术语"超弹性"。因此,超弹性镍-钛合金宏观上似乎相对于其他合金是非常有弹性的。当针对镍-钛合金使用时术语"拟弹性"和"超弹性"是同义的,并且术语"超弹性"用在本说明书中。

[0006]　形状记忆和超弹性镍-钛合金的独特性能的产生商业用途的能力部分地取决于在这些相变发生时的温度,即,该合金的A_s、A_f、M_s、M_f和M_d。例如,在诸如血管支架、血管过滤器和其他医疗设备的应用中,通常重要的是镍-钛合金在体温范围内(即,$A_f \leq \sim 37℃ \leq M_d$)呈现超弹性的特性。已经观察到,镍-钛合金的转变温度高度依赖于组成。例

如，已经观察到，镍-钛合金的转变温度对于该合金组成中的 1 原子百分比变化而言可以变化超过 100K。

[0007]　　另外，镍-钛合金的诸如致动器和可植入支架和其他医疗设备各种应用可被认为是疲劳关键的。疲劳是指当材料经受循环加载时发生的渐进的和局部的结构损坏。重复的加载和卸载导致微裂纹 (microscopic crack) 的形成，当在远低于材料的屈服强度或弹性极限的应力水平下对材料进一步实施循环加载时，所述微裂纹的尺寸可能增大。疲劳裂纹最终可能会达到临界尺寸，从而导致经受循环加载的材料的突然失效。已经观察疲劳裂纹容易在镍-钛合金中的非金属夹杂物 (inclusion) 和其他第二相处引发。因此，镍-钛合金的诸如致动器和可植入支架和其他医疗设备各种应用可被认为是夹杂物和第二相关键的。

[0008]　　概述

[0009]　　在一个非限制性实施方案中，用于生产镍-钛合金轧制产品的方法包括在低于 500℃ 的温度下冷加工镍-钛合金工件，以及热等静压压制 (HIP'ing) 所述冷加工的镍-钛合金工件。

[0010]　　在另一个非限制性实施方案中，用于生产镍-钛合金轧制产品的方法包括在大于或等于 500℃ 的温度下热加工镍-钛合金工件，然后在低于 500℃ 的温度下冷加工所述热加工的镍-钛合金工件。所述冷加工的镍-钛合金工件在于 700℃ 至 1000℃ 范围内的温度和 3,000psi 至 25,000psi 范围内的压力下操作的 HIP 炉中被热等静压压制 (HIP'ed) 至少 0.25 小时。

[0011]　　在另一个非限制性实施方案中，用于生产镍-钛合金轧制产品的方法包括在大于或等于 500℃ 的温度下热锻造镍-钛合金锭以产生镍-钛合金坯料 (billet)。所述镍-钛合金坯料在大于或等于 500℃ 温度下被热棒轧制以产生镍-钛合金工件。所述镍-钛合金工件在低于 500℃ 的温度下被冷拉拔以产生镍-钛合金棒。所述冷加工的镍-钛合金棒在于 700℃ 至 1000℃ 范围内的温度和 3,000psi 至 25,000psi 范围内的压力下操作的 HIP 炉中被热等静压压制至少 0.25 小时。

[0012]　　应该理解，在本说明书中公开并描述的本发明并不限定于总结于本概述中的实施方案。

附图说明

[0013]　　在本说明书中公开和描述的非限制性的和非详尽的实施方案的各种特点和特征可通过参考附图被更好地理解，其中：

[0014]　　图 1 是针对二元镍-钛合金的平衡相图；

[0015]　　图 2A 和图 2B 是示出了加工 (working) 对镍-钛合金微观结构中的非金属夹杂物和孔隙的影响；

[0016]　　图 3 是表示镍-钛合金中的非金属夹杂物以及相关的孔隙的扫描电子显微镜 (SEM) 图像（以背散射电子模式 (backscatter electron mode)500x 放大倍率）；

[0017]　　图 4A-4G 是按照本说明书中描述的实施方案进行处理的镍-钛合金的扫描电子显微镜图像（以背散射电子模式 500x 放大倍率）；

[0018]　　图 5A-5G 是按照本说明书中描述的实施方案进行处理的镍-钛合金的扫描电子显微镜图像（以背散射电子模式 500x 放大倍率）；

[0019]　　　图 6A-6H 是按照本说明书中描述的实施方案进行处理的镍－钛合金的扫描电子显微镜图像（以背散射电子模式 500x 放大倍率）；

[0020]　　　图 7A-7D 是按照本说明书中描述的实施方案进行处理的镍－钛合金的扫描电子显微镜图像（以背散射电子模式 500x 放大倍率）；和

[0021]　　　图 8A-8E 是按照本说明书中描述的实施方案进行处理的镍－钛合金的扫描电子显微镜图像（以背散射电子模式 500x 放大倍率）。

[0022]　　　当考虑根据本说明书的各种非限制性和非详尽的实施方案的以下详细描述时，读者将会理解前述细节及其他内容。

[0023]　　　详细描述

[0024]　　　本说明书描述和示出了各种实施方案，以提供对公开的生产镍－钛合金轧制产品的方法的功能、操作和实施的全面理解。应该理解，本说明书中描述和示出的各种实施方案是非限制性的和非详尽的。因此，本发明并不需要受本说明书中公开的各种非限制性和非详尽实施方案的描述的限制。针对各种实施方案示出和／或描述的特点和特征可以组合其他实施方案的特点和特征。这样的修改和变化意在包含在本说明书的范围内。正因为如此，可以修订本权利要求书，以详述本说明书中明确或固有描述的或以其他方式由本说明书明确或固有支持的任何特点或特征。此外，申请人保留修订本权利要求书的权利，以确定放弃现有技术中可能存在的特点或特征的权利要求。因此，任何这样的修订符合 35U. S. C. § §112(a) 和 132(a) 的要求。本说明书中公开和描述的各种实施方案可以包含本说明书中不同描述的特点和特征、由本说明书中不同描述的特点和特征组成或基本组成。

[0025]　　　此外，本说明书中所述的任何数值范围意在包括所有在所述范围内的相同数值精度的子范围。例如，"1. 0 至 10. 0"的范围意在包括在所述的 1. 0 最小值和所述的 10. 0 最大值之间（且包括这两个值）的所有子范围，也就是，其具有等于或大于 1. 0 的最小值和等于或小于 10. 0 的最大值，例如 2. 4 至 7. 6。本说明书中所述的任何最大数值限制意在包括所有其中包含的较小数值限制，且本说明书中所述的任何最小数值限制意在包括所有其中包含的较大数值限制。因此，申请人保留修订本说明书的权利，包括权利要求书，以明确详述包括在本文明确所述范围内的任何子范围。所有这样的范围意在固有地在本说明书中描述，以便明确详述对任何这样的子范围的修订符合 35U. S. C. § §112(a) 和 132(a) 的要求。

[0026]　　　除非另有说明，本文认定的任何专利、出版物或其他公开材料全部通过引用的方式并入本说明书，但仅至所并入的材料与本说明书中的现有描述、定义、说明或其他明确阐述的公开材料不发生冲突的程度。正因为如此，且在必要的程度，本说明书中阐述的明确公开将替代通过引用并入本文的任何冲突材料。据称通过引用并入本说明书但其与本文阐述的现有定义、说明或其他公开材料存在冲突的任何材料或其部分，仅并入至在并入的材料和现有公开材料之间不会发生冲突的程度。申请人保留修订本说明书的权利，以明确详述通过引用并入本文的任何主题或其部分。

[0027]　　　本说明书中使用的语法冠词"一 (one)"、"一个 (a)"、"一个 (an)"和"该 (the)"意在包括"至少一个"或"一个或多个"，除非另有说明。因此，本说明书中使用的冠词是指该冠词的语法对象中的一个或多个（即，指"至少一个"）。通过实施说明，"一组件"是指一个或多个组件，且因此，可能考虑多个的组件，且在所述实施方案的实施中可以采用或使用所述多个的组件。另外，单数名词的使用包括复数，且复数名词的使用包括单数，除非使用

的上下文另有要求。

[0028]　　在本说明书中描述的各种实施方案涉及用于制备镍－钛合金轧制产品的方法,所述轧制产品具有改善的微观结构,例如非金属夹杂物和孔隙的降低的面积分率和尺寸。如本文所用,术语"轧制产品"是指通过合金锭的热机械加工生产的合金制品。轧制产品包括,但不限于,坯料、棒、杆、线、管、厚板(slab)、板(plate)、片材和箔。此外,如本文中所使用的,术语"镍－钛合金"是指合金组合物,其含有基于所述合金组合物的总重量的至少35%的钛和至少45%的镍。在各种实施方案中,在本说明书中描述的方法适用于近等原子的镍－钛合金。如本文所使用的,术语"近等原子的镍－钛合金"是指的合金含有45.0原子%至55.0原子%的镍、余量钛和残余杂质。近等原子的镍－钛合金包括基本由基于原子50%的镍和50%的钛组成的等原子的二元镍－钛合金。

[0029]　　镍－钛合金轧制产品可以由包括例如以下步骤的方法制备:使用诸如真空感应熔炼(VIM)和/或真空电弧重熔(VAR)的熔炼技术配制合金化学;铸造镍－钛合金锭;将铸造的锭锻造成坯料;将所述坯料热加工成轧制料(mill stock)形式;将所述轧制料形式冷加工(及任选的中间退火)成轧制产品形式;和将所述轧制产品形式轧机退火,以生产最终的轧制产品。这些过程可能会产生具有可变的微观结构如显微纯洁度(microcleanliness)的轧制产品。如本文所用,术语"显微纯洁度"是指镍－钛合金的如ASTM F 2063-12:Standard Specification for Wrought Nickel-Titanium Shape Memory Alloys for Medical Devices and Surgical Implants 的第9.2节中所定义的非金属夹杂物和孔隙特性,其通过引用的方式并入本说明书中。对于镍－钛合金轧制产品生产者而言,生产始终如一地满足诸如ASTM F 2063-12规定的行业标准的显微纯洁度和其他要求的镍－钛合金轧制产品在商业上是重要的。

[0030]　　本说明书中所描述的方法包括在低于500℃的温度下冷加工镍－钛合金工件,和热等静压压制所述冷加工的镍－钛合金工件。冷加工降低了镍－钛合金工件中的非金属夹杂物的尺寸和面积分率。热等静压压制减少或消除了镍－钛合金工件中的孔隙。

[0031]　　通常,术语"冷加工"指是在低于材料的流动应力被显著降低时的温度的温度下加工合金。针对所公开的方法如本文所用,"冷加工"、"冷加工的"、"冷成型"、"冷轧"和类似的术语(或针对特定加工或成型技术使用的"冷",例如"冷拉拔")是指在低于500℃的温度下加工或已经加工过的状态,视具体情况而定。当工件的内部和/或表面温度低于500℃时,可以执行冷加工操作。冷加工操作可在低于500℃的任意温度下进行,例如,低于400℃、低于300℃、低于200℃或低于100℃。在各种实施方案中,冷加工操作可以在环境温度下进行。在给定的冷加工操作中,镍－钛合金工件的内部和/或表面温度可能在加工期间因绝热加热而上升超出指定的限制(例如,500℃或100℃);然而,为本说明书中所描述的方法的目的,所述操作仍是冷加工操作。

[0032]　　一般地,热等静压压制(HIP或HIP'ing)是指在HIP炉中高压和高温气体(例如氩气)至工件的外表面的等静压(即均一)施加。针对所公开的方法如本文所用,"热等静压压制","热等静压压制的"和类似的术语或缩写词是指高压和高温气体至冷加工的状态中的镍－钛合金工件的等静压施加。在各种实施方案中,镍－钛合金工件可以在于700℃至1000℃范围内的温度和3,000psi至50,000psi范围内的压力下操作的HIP炉中被热等静压压制。在一些实施方案中,镍－钛合金工件可以在于750℃至950℃、800℃至950℃、

800℃至900℃或850℃至900℃范围内的温度;和在7,500psi至50,000psi、10,000psi至45,000psi、10,000psi至25,000psi、10,000psi至20,000psi、10,000psi至17,000psi、12,000psi至17,000psi或12,000psi至15,000psi范围内的压力下操作的HIP炉中被热等静压压制。在各种实施方案中,镍－钛合金工件可以在温度和压力下在HIP炉中被热等静压压制至少0.25小时,并且在一些实施方案中,被热等静压压制至少0.5小时、0.75小时、1.0小时、1.5小时或至少为2.0小时。

[0033]　　如本文所用,术语"非金属夹杂物"是指在含有非金属成分（如碳和／或氧原子）的NiTi金属基体中的次要相。非金属夹杂物包括$Ti_4Ni_2O_x$氧化物非金属夹杂物和碳化钛(TiC)两者和／或碳氧化钛(Ti(C,O))非金属夹杂物。非金属夹杂物不包括离散的金属间相(inter-metallic phase),例如,Ni_4Ti_3、Ni_3Ti_2、Ni_3Ti和Ti_2Ni,其也可形成在近等原子的镍－钛合金中。

[0034]　　基本上由基于原子50％的镍和50％的钛组成（按重量计大约55％的Ni、45％的Ti）的等原子的镍－钛合金具有基本上由NiTi B2立方结构（即,氯化铯型结构）构成的奥氏体相。与形状记忆效应和超弹性相关的马氏体相变是无扩散的,并且马氏体相具有B19的单斜晶结构。NiTi相位区是很窄的,并基本上相当于在低于约650℃的温度下的等原子的镍－钛。参见图1。在富Ti侧上的NiTi相位区边界基本上从环境温度垂直地高至约600℃。在富Ni侧上的NiTi相位区边界随着温度的下降而减少,并且镍在约600℃及以下在B2Ni-Ti中的溶解度是可忽略的。因此,近等原子的镍－钛合金通常含有金属间第二相（例如,Ni_4Ti_3、Ni_3Ti_2、Ni_3Ti和Ti_2Ni),其化学特性取决于近等原子的镍－钛合金是否是富Ti的或富Ni的。

[0035]　　如前所述,镍－钛合金锭可以由使用真空感应熔炼(VIM)熔化的熔融合金铸造。可以将钛输入材料和镍输入材料放置在VIM炉中的石墨坩埚中,并熔化以产生熔融的镍－钛合金。在熔化期间,来自石墨坩埚的碳可能溶解在所述熔融的合金中。在镍－钛合金锭的铸造过程中,碳可以与所述熔融的合金反应,产生形成铸锭中的非金属夹杂物的立方碳化钛(TiC)和／或立方碳氧化钛(Ti(C,O))颗粒。VIM锭通常可含有按重量计100-800ppm的碳和按重量计100-400ppm的氧,这可能在镍－钛合金基体中产生相对较大的非金属夹杂物。

[0036]　　镍－钛合金锭也可以由使用真空电弧重熔(VAR)熔化的熔融合金制造。在这方面,术语VAR可能是用词不当,因为钛输入材料和镍输入材料可以被熔化在一起,以在VAR炉中首先形成合金组合物,在这种情况下的操作可更精确地称为真空电弧熔炼。为了保持一致性,术语"真空电弧重熔"和"VAR"被用在本说明书中,以表示通过元素输入材料或其他的进料的合金重熔和初始合金熔化这两者,在给定的操作中可能视情况而定。

[0037]　　钛输入材料和镍输入材料可以用于以机械方式形成电极,所述电极在VAR炉中被真空电弧重熔在水冷铜坩埚中。相对于使用需要石墨坩埚的VIM熔化的镍－钛合金而言,水冷铜坩埚的使用可以显著地降低渗碳(carbon pickup)的水平。VAR锭通常可包含按重量计小于100ppm的碳,这显著地降低或消除碳化钛(TiC)和／或碳氧化钛(Ti(C,O))非金属夹杂物的形成。然而,当由海绵钛输入材料制成时,VAR锭通常可含有例如按重量计100-400ppm的氧。氧可以与熔融合金反应,产生例如$Ti_4Ni_2O_x$氧化物非金属夹杂物,它们作为通常存在于富Ti的接近等原子的镍－钛合金中的Ti_2Ni金属间第二相具有几乎相同的立方结构（空间群Fd3m)。这些非金属氧化物夹杂物甚至在通过低氧（按重量计<60ppm)碘

化物还原的钛晶棒熔化的高纯度 VAR 锭中被观察到。

[0038]　　铸造的镍－钛合金锭和通过所述锭制成的制品可以在镍－钛合金基体中包含相对较大的非金属夹杂物。这些大的非金属夹杂物颗粒可能对镍－钛合金制品、特别是近等原子的镍－钛合金制品的疲劳寿命和表面质量有不利影响。实际上，行业标准规则上对旨在用于疲劳关键的和表面质量关键的应用（例如，致动器、可植入的支架和其他医疗设备）中的镍－钛合金中的非金属夹杂物的尺寸和面积分率实施了严格的限制。参见 ASTM F 2063-12 :Standard Specification for Wrought Nickel-Titanium Shape Memory Alloys for Medical Devices and Surgical Implants,其通过引用的方式并入本说明书中。因此，将镍－钛合金轧制产品中的非金属夹杂物的尺寸和面积分率最小化可能是重要的。

[0039]　　形成在铸造的镍－钛合金中的非金属夹杂物通常是易碎的和破裂的，并在材料的加工期间移动。非金属夹杂物在加工操作期间的破裂、伸长和运动降低了镍－钛合金中的非金属夹杂物的尺寸。然而，非金属夹杂物在加工操作期间的破裂和移动还可同时导致微观空隙的形成，这增加了主体材料中的孔隙。这种现象示于图 2A 和图 2B 中，其示意性地示出了加工对非金属夹杂物和镍－钛合金微观结构中的孔隙的反作用。图 2A 示出了含有非金属夹杂物 10 但缺乏孔隙的镍－钛合金的微观结构。图 2B 示出了加工对非金属夹杂物 10' 的作用，所述夹杂物显示出被破裂成更小的颗粒并被隔开，但其中增加的孔隙 20 相互连接所述更小的夹杂物颗粒。图 3 是示出了镍－钛合金中的非金属夹杂物和相关的孔隙空隙的实际的扫描电子显微镜（SEM）图像（以背散射电子模式 500x 放大倍率）。

[0040]　　与非金属夹杂物类似，在镍－钛合金中的孔隙可能对镍－钛合金制品的疲劳寿命和表面质量产生不利的影响。实际上，行业标准规则也对旨在用于疲劳关键的和表面质量关键的应用（例如，致动器、可植入支架等医疗设备）中的镍－钛合金中的孔隙实施了严格的限制。参见 ASTM F 2063-12 :Standard Specification for Wrought Nickel-Titanium Shape Memory Alloys for Medical Devices and Surgical Implants。

[0041]　　具体地，根据 ASTM F2063-12 规则，对于具有低于或等于 $30^{\circ}C$ 的 A_s 的近等原子的镍－钛合金而言，孔隙和非金属夹杂物的最大允许长度尺寸是 39.0 微米（0.0015 英寸），其中，所述长度包括邻接的颗粒和空隙以及通过空隙隔开的颗粒。此外，孔隙和非金属夹杂物不能构成镍－钛合金微观结构的大于 2.8%（面积百分比），当在视野的任意区域中以 400x 到 500x 的放大倍率观察时。这些测量可以按照 ASTM E1245-03(2008)-Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals by Automatic Image Analysis（其通过引用的方式并入本说明书中）或等效的方法进行。

[0042]　　参考图 2A 和图 2B,尽管加工镍－钛合金可以降低非金属夹杂物的尺寸，但是最终结果可能是增加非金属夹杂物结合孔隙的总的尺寸和面积分率。因此，满足工业标准如 ASTM F 2063-12 规则的严格限制的镍－钛合金材料的一致和高效的生产已被证实是镍－钛合金轧制产品的生产者的一种挑战。本说明书中所描述的方法通过提供具有改善的微观结构（包括非金属夹杂物和孔隙二者的降低的尺寸和面积分率）的镍－钛合金轧制产品满足这一挑战。例如，在各种实施方案中，通过本说明书中所描述的方法制得的镍－钛合金轧制产品符合 ASTM F 2063-12 标准规则的要求，仅在冷加工后进行测量。

[0043]　　如前所述，用于生产镍－钛合金轧制产品的方法可包括冷加工和热等静压压制镍－钛合金工件。镍－钛合金工件在低于 $500^{\circ}C$ 的温度下（例如，在环境温度下）的冷加

工,例如,有效地使非金属夹杂物破裂并沿着所施加的冷加工的方向移动,并降低在镍－钛合金工件中的非金属夹杂物的尺寸。在任何最终的热加工操作都已完成之后,冷加工可以施加至镍－钛合金工件。在一般情况下,"热加工"是指在大于材料的流动应力显著降低时的温度的温度下加工合金。针对所描述的方法如本文所用,"热加工"、"热加工的"、"热锻造"、"热轧"和类似的术语(或针对特定加工或成型技术使用的"热")是指在大于或等于500℃的温度下加工或已经加工过的状态,视具体情况而定。

[0044]　　在各种实施方案中,用于生产镍－钛合金轧制产品的方法可包括在冷加工操作之前的热加工操作。如上所述,镍－钛合金可以使用 VIM 和／或 VAR 由镍输入材料和钛输入材料铸造而成,以产生镍－钛合金锭。铸造的镍－钛合金锭可以被热加工,以产生坯料。例如,在各种实施方案中,具有在 10.0 英寸至 30.0 英寸范围内的直径的铸造的镍－钛合金锭(工件)可以被热加工(例如,通过热旋锻),以产生具有在 2.5 英寸至 8.0 英寸范围内的直径的坯料。镍－钛合金坯料(工件)可以是热棒轧制的,例如,以产生具有 0.218 英寸至 3.7 英寸范围内的直径的棒料或杆料。镍－钛合金棒料或杆料(工件)可以被热拉拔,例如,以产生具有在 0.001 英寸至 0.218 英寸范围内的直径的镍－钛合金棒、杆或线。在任意的热加工操作之后,镍－钛合金轧制产品(以中间体(intermediate)形式)可以按照本说明书中描述的实施方案冷加工,以产生镍－钛合金轧制产品的最终宏观结构形式。如本文所用,相比于表示合金材料的微观晶粒结构和相位结构(包括夹杂物和孔隙度)的"微观结构"而言,术语"宏观结构"或"宏观结构的"是指合金工件或轧制产品的宏观形状和尺寸。

[0045]　　在各种实施方案中,可以使用包括但不限于锻造、镦粗、拉拔、轧制、挤出、皮尔格式轧制(pilgering)、摆辗、型锻、顶锻、压印和它们的组合的成型技术对铸造的镍－钛合金锭进行热加工。一个或多个热加工操作可被用于将铸造的镍－钛合金锭转变成半成品或中间轧制产品(工件)。中间轧制产品(工件)可以随后使用一个或多个的冷加工操作被冷加工成轧制产品的最终宏观结构形式。冷加工可以包括但不限于锻造、镦粗、拉拔、轧制、挤出、皮尔格式轧制、摆辗、型锻、顶锻、压印和它们中的任意组合。在各种实施方案中,镍－钛合金工件(例如,锭、坯料或其他轧制产品料形式)可以采用至少一种热加工技术被热加工,并随后使用至少一种冷加工技术被冷加工。在各种实施方案中,可在 500℃至 1000℃的范围或任何被包含在其中的子范围(例如,600℃至 900℃和 700℃至 900℃)内的初始内部温度或表面温度下在镍－钛合金工件上实施热加工。在各种实施方案中,例如,可在低于500℃的初始内部温度或表面温度(例如环境温度)下在镍－钛合金制品上实施冷加工。

[0046]　　通过举例的方式,铸造的镍－钛合金锭可以是热锻造的以产生镍－钛合金坯料。镍－钛合金坯料可以是热棒轧制的,例如,以产生具有比为杆或棒轧制产品指定的最终直径更大的直径的镍－钛合金圆棒料。较大直径的镍－钛合金圆棒料可以是半成品的轧制产物或中间工件即随后冷拔,例如,以产生具有最终指定直径的杆或棒轧制产品。镍－钛合金工件的冷加工可以使非金属夹杂物破裂并沿拉拔方向移动,并降低工件中的非金属夹杂物的尺寸。冷加工也可以增加镍－钛合金工件中的孔隙,增加至任意因先前的热加工操作导致存在于工件中的孔隙。随后的热等静压压制操作可减少或完全消除镍－钛合金工件中的孔隙。随后的热等静压压制操作也可以同时使镍－钛合金工件再结晶和／或为所述工件提供应力消除退火。

[0047]　　镍－钛合金呈现出迅速的冷加工硬化，并因此可在连续的冷加工操作之后对冷加工的镍－钛合金制品进行退火。例如，用于生产镍－钛合金轧制产品的方法可包括在第一冷加工操作中对镍－钛合金工件冷加工，对所述冷加工的镍－钛合金工件进行退火，在第二冷加工操作中对所述退火的镍－钛合金工件冷加工和热等静压压制所述两次冷加工的镍－钛合金工件。在所述第二冷加工操作之后和所述热等静压压制操作之前，所述镍－钛合金工件可经受至少一个额外的退火操作，以及至少一个额外的冷加工操作。在所述第一冷加工操作和所述热等静压压制操作之间的中间退火和冷加工的连续周期的数目可以通过要投入所述工件上的冷加工量与特定的镍－钛合金组成的加工硬化速率来确定。连续的冷加工操作之间的中间退火可以在700℃至900℃或750℃到850℃的范围内的温度下操作的炉子中实施。连续的冷加工操作之间的中间退火可以实施至少20秒、长至2小时或更多的炉时间，这取决于材料的尺寸和炉子的类型。

[0048]　　在各种实施方案中，可以实施热加工和／或冷加工操作，以产生镍－钛合金轧制产品的最终宏观结构形式，并且还可以在冷加工的工件上实施随后的热等静压压制操作，以产生镍－钛合金轧制产品的最终微观结构形式。与使用热等静压压制用于冶金粉末的整合和烧结不同，在本说明书中描述的方法中的热等静压压制的使用不会导致冷加工的镍－钛合金工件中的宏观尺寸或形状变化。

[0049]　　尽管不希望受理论的束缚，但据信在使所述镍－钛合金中的易碎（即，硬和非延展性）的非金属夹杂物破裂和移动、从而降低非金属夹杂物的尺寸方面，冷加工比热加工显著更有效。在加工操作期间，输入到镍－钛合金材料中的应变能引起较大的非金属夹杂物断裂成以应变的方向分散开的更小的夹杂物。在在升高的温度下的热加工期间，镍－钛合金材料的塑性流动应力是显著更低的；因此，该材料更容易围绕夹杂物流动，并且不会将尽可能多的应变输入该夹杂物中，导致断裂和移动。然而，在热加工期间，合金材料相对于夹杂物的塑性流动仍在夹杂物和镍－钛合金材料之间产生空隙空间，从而增加了材料的孔隙。另一方面，在冷加工期间，镍－钛合金材料的塑性流动应力是显著更大的，并且该材料不会那样容易地围绕夹杂物塑性地流动。因此，显著多个应变能量被输入该夹杂物中，导致断裂和移动，这显著地增加了夹杂物的断裂、移动、尺寸减小和面积减小的速率，但是也增加了形成空隙和孔隙的速率。如先前所描述的，但是，尽管对镍－钛合金的加工可以降低非金属夹杂物的尺寸和面积分率，但是最终结果可能是增加非金属夹杂物结合孔隙的总的尺寸和面积分率。

[0050]　　本发明人已经发现，热等静压压制热加工的和／或冷加工的镍－钛合金工件将有效地闭合（即，"愈合"）在热加工和／或冷加工操作过程中形成的合金中的孔隙。热等静压压制使合金材料在微观尺度上塑性地屈服和闭合形成镍－钛合金中的内部孔隙的空隙空间。以这种方式，热等静压压制允许镍－钛合金材料在空隙空间中的微蠕变。另外，由于孔隙空隙的内表面没有被暴露于大气中，当表面通过HIP操作的压力走到一起时形成冶金结合。这导致非金属夹杂物的尺寸和面积分率的减少，所述非金属夹杂物通过镍－钛合金原料而不是空隙空间隔开。这是用于生产符合ASTM F2063-12标准规则对在冷加工之后测量的尺寸和面积分率的要求的镍－钛合金轧制产品是特别有利的，该标准规则连续的非金属夹杂物和孔隙空隙的聚集尺寸和面积分率设置了严格的限制（39.0微米（0.0015英寸）的最大允许长度尺寸），以及2.8％的最大面积分率）。

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[0051]　　在各种实施方案中,热等静压压制操作可以实现多种功能。例如,热等静压压制操作可以减少或消除热加工和／或冷加工的镍－钛合金中的孔隙,而热等静压压制操作可以同时使所述镍－钛合金退火,从而减轻被先前的冷加工操作诱导出的任何内部应力,并且在一些实施方案中,使所述合金重结晶以达到所期望的晶粒结构,例如,4 或更大的 ASTM晶粒尺寸号 (G)（根据 ASTM E112-12 :Standard Test Methods for Determining Average Grain Size 测量,其通过引用并入本说明书中）。在各种实施方案中,在热等静压压制之后,镍－钛合金轧制产品可以经过一个或多个精加工 (finishing) 操作,包括但不限于剥离、抛光、无心磨削、喷砂、酸洗、矫直、上浆、珩磨或其他表面调整操作。

[0052]　　在各种实施方案中,通过本说明书中所描述的方法制得的轧制产品可以包括,例如,坯料、杆、棒、管、厚板、板、片材、箔或线。

[0053]　　在各种实施方案中,镍输入材料和钛输入材料可以被真空电弧重熔以产生按照本说明书中所描述的实施方案被热加工和／或冷加工和热等静压压制的镍－钛合金 VAR 锭。镍输入材料可以包括例如电解镍或镍粉,并且钛输入材料可以选自由海绵钛、电解钛晶体、钛粉和碘化物还原钛晶棒组成的组。在镍输入材料和钛输入材料被熔合在一起以形成镍钛合金之前,镍输入材料和／或钛输入材料可以包括例如通过电子束熔炼已被精制的不太纯的形式的元素镍或元素钛。除镍和钛之外的熔合元素,如果存在的话,也可以使用在冶金领域中已知的元素输入材料加入。镍输入材料和钛输入材料（和任何其他有意的合金输入材料）可被机械地压紧在一起,以产生用于初始的 VAR 操作的输入电极。

[0054]　　通过将测定的量的镍输入材料和钛输入材料包括在用于初始的 VAR 操作的输入电极中,可以将初始的近等原子的镍－钛合金组合物尽可能准确地熔化至预定的组成（例如,50.8 原子％（约 55.8 重量％）的镍、余量钛和残余杂质）。在各种实施方案中,初始的近等原子的镍－钛合金组成的精度可以通过测量 VAR 锭的转变温度评估,例如,通过测量合金的 A_s、A_f、M_s、M_f 和 M_d 中的至少一个。

[0055]　　已经观察到,镍－钛合金的转变温度在很大程度上取决于该合金的化学组成。特别是,已经观察到,镍－钛合金的 NiTi 相中的溶液中的镍量将强烈地影响该合金的转变温度。例如,镍－钛合金的 M_s 将通常随着 NiTi 相中增加的固溶态镍的浓度而降低 ;而镍－钛合金的 M_s 将通常随着 NiTi 相中降低的固溶态镍的浓度而增加。对于给定的合金组合物,镍－钛合金的转变温度被很好地表征。正因为如此,转变温度的测量以及测得的值与对应于该合金的目标化学组成的预期值的比较,可用于确定与该合金的目标化学组成的任何偏差。

[0056]　　可以测量 VAR 锭或其他中间或最终轧制产品的转变温度,例如,使用差示扫描量热法 (DSC) 或等效的热机械试验方法。在各种实施方案中,近等原子的镍－钛合金 VAR锭的转变温度可以按照 ASTM F2004-05 :Standard Test Method for Transformation Temperature of Nickel-Titanium Alloys by Thermal Analysis 测量,其通过引用并入本说明书中。VAR 锭或其他中间或最终轧制产品的转变温度还可以,例如根据 ASTMF2082-06 :Standard Test Method for Determination of Transformation Temperatureof Nickel-Titanium Shape Memory Alloys by Bend and Free Recovery 使用弯曲自由回复 (BFR) 测试测量,其通过引用并入本说明书中。

[0057]　　当测定的转变温度偏离于针对目标合金组合物的期望的转变温度预定的规格时,

初始 VAR 锭可以在第二 VAR 操作中通过镍输入材料、钛输入材料或具有已知转变温度的镍－钛母合金(master alloy)的矫正加料(corrective addition)被重新熔化。可以测量所得的第二镍－钛合金 VAR 锭的转变温度以确定该转变温度是否落在针对目标合金组合物的预期转变温度预定的规格内。该预定的规范可以是关于目标组合物的预期转变温度的温度范围。

[0058]　　如果测得的第二镍－钛 VAR 锭的转变温度落在预定的规格内,则所述第二 VAR 锭以及在必要时的随后的 VAR 锭可以在连续的 VAR 操作中通过矫正的熔合加料再熔化,直到测得的转变温度落在预定的规格内。这种重复的再熔化和熔合实践实现了对近等原子的镍－钛合金组成和相变温度的准确和精确控制。在各种实施方案中,A_f、A_s 和／或 A_p 被用于重复地重新熔化和熔合近等原子的镍－钛合金(奥氏体峰温度(A_p)是镍－钛形状记忆或超弹性的合金展示出由马氏体相变至奥氏体的最高速率时的温度,参见 ASTM F 2005-05：Standard Terminology for Nickel-Titanium Shape Memory Alloys,其通过引用并入本说明书中)。

[0059]　　在各种实施方案中,钛输入材料和镍输入材料可以被真空感应熔化,以产生镍－钛合金,并且所述镍－钛合金的锭可以由 VIM 熔体铸造而成。所述 VIM 铸锭可以按照本说明书中描述的实施方案被热加工和／或冷加工和热等静压压制。镍输入材料可以包括例如电解镍或镍粉,并且钛输入材料可以选自由海绵钛、电解钛晶体、钛粉和碘化物还原钛晶棒组成的组。可以将镍输入材料和钛输入材料装入 VIM 坩埚中,熔化在一起,并被铸造成初始的 VIM 锭。

[0060]　　通过将测定的量的镍输入材料和钛输入材料包括在至 VIM 坩埚的装料中,可以将初始的近等原子的镍－钛合金组合物尽可能准确地熔化至预定的组成(例如,50.8 原子％(大约 55.8 重量％)的镍、钛和残余杂质)。在各种实施方案中,初始的近等原子的镍－钛合金组成的精度可以通过测量 VIM 锭或其它中间或最终轧制产品的转变温度评估,如上文针对使用 VAR 制备的镍钛合金所述的那样。如果测得的转变温度落在预定的规格之外,则初始的 VIM 锭以及在必要时的随后的 VIM 锭或其它中间或最终轧制产品可以在连续的 VIM 操作中通过矫正的熔合加料再熔化,直到测得的转变温度落在预定的规格内。

[0061]　　在各种实施方案中,可以使用一个或多个 VIM 操作和一个或多个 VAR 操作的组合生产镍－钛合金。例如,镍－钛合金锭可以使用 VIM 操作由镍输入材料和钛输入材料制备以制备初始锭,所述初始锭然后在 VAR 操作中被重熔。当其中多个 VIM 锭被用于构造 VAR 电极时,还可以使用绑定的 VAR 操作。

[0062]　　在各种实施方案中,镍－钛合金可以包含 45.0 原子％至 55.0 原子％的镍、余量钛和残余杂质。镍－钛合金可以包含 45.0 原子％至 56.0 原子％的镍或任何被包含在其中的子范围(例如,49.0 原子％至 52.0 原子％)的镍。镍－钛合金也可包含 50.8 原子％的镍(±0.5、±0.4、±0.3、±0.2 或 ±0.1 原子％的镍)、余量钛和残余杂质。镍－钛合金也可包含 55.04 原子％的镍(±0.10、±0.05、±0.04、±0.03、±0.02 或 ±0.01 原子％的镍)、余量钛和残余杂质。

[0063]　　在各种实施方案中,镍－钛合金可以包含 50.0 重量％至 60.0 重量％的镍、余量钛和残余杂质。镍－钛合金可以包含 50.0 重量％至 60.0 重量％的镍或任何被包含在其中的子范围(例如,54.2 重量％至 57.0 重量％)的镍。镍－钛合金可以包含 55.8％重量的镍

（±0.5、±0.4、±0.3、±0.2 或 ±0.1%重量的镍）、余量钛和残余杂质。镍－钛合金可以包含 54.5%重量的镍（±2、±1、±0.5、±0.4、±0.3、±0.2 或 ±0.1 重量%的镍）、余量钛和残余杂质。

[0064]　　在本说明书中描述的各种实施方案也适用于形状记忆或超弹性镍－钛合金，所述合金包括至少一种除镍和钛之外的熔合元素，例如，铜、铁、钴、铌、铬，铪、锆、铂和／或钯。在各种实施方案中，形状记忆或超弹性镍－钛合金可包括镍、钛、残余杂质和 1.0 原子%至 30.0 原子%的至少一种其他合金元素，例如，铜、铁、钴、铌、铬、铪、锆、铂和钯。例如，形状记忆或超弹性镍－钛合金可包括镍、钛、残余杂质和 5.0 原子%至 30.0 原子%的铪、锆、铂、钯或它们的任意组合。在各种实施方案中，形状记忆或超弹性镍－钛合金可包括镍、钛、残余杂质和 1.0 原子%至 5.0 原子%的铜、铁、钴、铌、铬、或它们的任意组合。

[0065]　　下列非限制性和非详尽实施例意在进一步描述各种非限制性和非详尽实施方案，而不限制本说明书中描述的实施方案的范围。

实施例

[0066]　　实施例 1：

[0067]　　将 0.5 英寸直径的镍－钛合金棒切割成七（7）条样品。将切片分别如表 1 所示的那样进行处理。

[0068]　　表 1

[0069]

样品号	处理
1	无
2	HIP'ed:800℃;15,000psi;2 小时
3	HIP'ed:850℃;15,000psi;2 小时
4	HIP'ed:900℃;15,000psi;2 小时
5	HIP'ed:800℃;45,000psi;2 小时
6	HIP'ed:850℃;45,000psi;2 小时
7	HIP'ed:900℃;45,000psi;2 小时

[0070]　　在热等静压压制处理之后，将样品 2-7 分别在样品的近似中心线处纵向切片，以产生用于扫描电子显微镜（SEM）的样品。样品 1 如接收时原样地被纵向切开，没有任何热等静压压制处理。按照 ASTM E1245-03(2008)-Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals by Automatic Image Analysis 测量连续的非金属夹杂物和孔隙空隙的最大尺寸和面积分率。使用 SEM 以背散射电子模式检查全纵向的横截面。对与每个切片样品而言，含有连续的非金属夹杂物和孔隙的三个最大可见区域的 SEM 场以 500 倍的放大倍率进行成像。图像分析软件用来测量在每

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个切片样品的三个 SEM 图像中的非金属夹杂物和孔隙的最大尺寸和面积分率。结果列于表 2 和表 3。

[0071]　表 2

[0072]

样品号	最大夹杂物尺寸 (微米)	最大面积分率 (%)	对应于最大夹杂物尺寸的 SEM 图像
1	51.5	1.88	图 4A
2	43.6	2.06	图 4B
3	35.9	1.44	图 4C
4	29.4	1.46	图 4D
5	32.1	1.87	图 4E
6	29.4	1.86	图 4F
7	38.8	1.84	图 4G

[0073]　表 3

[0074]

样品号	三个最大夹杂物尺寸的平均(微米)	三个最大面积分率的平均(%)
1	49.1	1.57
2	39.3	1.73
3	33.8	1.28
4	27.7	1.18
5	30.1	1.42
6	28.8	1.49
7	34.8	1.55

[0075]　结果表明,热等静压压制操作总体上降低了非金属夹杂物和孔隙的组合的尺寸和面积分率。热等静压压制的镍－钛合金棒总体上满足 ASTM F 2063-12 标准规则的要求 (39.0 微米 (0.0015 英寸) 的最大允许长度尺寸,和 2.8% 的最大面积分率)。图 4B-4G 与图 4A 的比较表明,热等静压压制操作减少了并且在某些情况下消除了镍－钛合金棒中的孔隙。

[0076]　实施例 2:

[0077]　将 0.5 英寸直径的镍－钛合金棒切割成七 (7) 条样品。将样品分别如表 4 所示的那样进行处理。

[0078]　表 4

[0079]

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样品号	处理
1	无
2	HIP'ed:800℃;15,000psi;2 小时
3	HIP'ed:850℃;15,000psi;2 小时
4	HIP'ed:900℃;15,000psi;2 小时
5	HIP'ed:800℃;45,000psi;2 小时
6	HIP'ed:850℃;45,000psi;2 小时
7	HIP'ed:900℃;45,000psi;2 小时

[0080]　　　在热等静压压制处理之后,将样品 2-7 分别在样品的近似中心线处纵向切片,以产生用于扫描电子显微镜 (SEM) 的样品。样品 1 如接收时原样地被纵向切开,没有任何热等静压压制处理。按照 ASTM E1245-03(2008)-Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals by Automatic Image Analysis 测量连续的非金属夹杂物和孔隙空隙的最大尺寸和面积分率。使用 SEM 以背散射电子模式检查全纵向的横截面。对与每个切片样品而言,含有连续的非金属夹杂物和孔隙的三个最大可见区域的 SEM 场以 500 倍的放大倍率进行成像。图像分析软件用来测量在每个切片样品的三个 SEM 图像中的非金属夹杂物和孔隙的最大尺寸和面积分率。结果列于表 5 和表 6。

[0081]　　表 5

[0082]

样品号	最大夹杂物尺寸 (微米)	最大面积分率 (%)	对应于最大夹杂物尺寸的 SEM 图像
1	52.9	1.63	图 5A
2	41.7	1.23	图 5B
3	28.3	1.63	图 5C
4	29.9	0.85	图 5D
5	34.1	0.95	图 5E
6	30.2	1.12	图 5F
7	34.7	1.25	图 5G

[0083]　　表 6

[0084]

样品号	三个最大夹杂物尺寸的平均(微米)	三个最大面积分率的平均(%)
1	49.0	1.45
2	37.0	1.15
3	27.8	1.28
4	27.9	0.80
5	32.8	0.88
6	29.0	1.05
7	33.1	1.11

[0085]　　　结果表明,热等静压压制操作总体上降低了非金属夹杂物和孔隙的组合的尺寸和面积分率。热等静压压制的镍－钛合金棒总体上满足 ASTM F 2063-12 标准规则的要求(39.0 微米(0.0015 英寸)的最大允许长度尺寸,和 2.8% 的最大面积分率)。图 5B-5G 与图 5A 的比较表明,热等静压压制操作减少了并且在某些情况下消除了镍－钛合金棒中的孔隙。

[0086]　　实施例 3:

[0087]　　　将 0.5 英寸直径的镍－钛合金棒在 900℃ 和 15,000psi 下热等静压压制 2 小时。将热等静压压制棒纵向切片,以产生八(8)个用于扫描电子显微镜(SEM)的纵向样品切片。按照 ASTM E1245-03(2008)-Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals by Automatic Image Analysis 测量连续的非金属夹杂物和孔隙空隙的最大尺寸和面积分率。使用 SEM 以背散射电子模式对八个纵向横截面中的每一个进行检查。对与每个样品切片而言,含有连续的非金属夹杂物和孔隙的三个最大可见区域的 SEM 场以 500 倍的放大倍率进行成像。图像分析软件用来测量在每个样品切片的三个 SEM 图像中的非金属夹杂物和孔隙的最大尺寸和面积分率。结果列于表 7。

[0088]　　表 7

[0089]

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样品切片	最大夹杂物尺寸 (微米)	最大面积分率 (%)	对应于最大夹杂物尺寸的 SEM 图像
1	34.7	1.15	图 6A
2	29.0	1.09	图 6B
3	28.7	1.23	图 6C
4	34.7	1.20	图 6D
5	32.8	1.42	图 6E
6	28.3	1.23	图 6F
7	35.4	0.95	图 6G
8	34.4	1.03	图 6H
平均	32.3	1.20	---

[0090]　　　结果表明,热等静压压制的镍 - 钛合金棒总体上满足 ASTM F2063-12 标准规则的要求 (39.0 微米 (0.0015 英寸) 的最大允许长度尺寸,和 2.8% 的最大面积分率)。图 6A-6H 的研究表明,热等静压压制操作消除了镍 - 钛合金棒中的孔隙。

[0091]　　　实施例 4:

[0092]　　　两 (2) 个 4.0 英寸直径的镍 - 钛合金坯料 (坯料 -A 和坯料 -B) 分别被切成两 (2) 个更小的坯料,以产生总共四 (4) 个坯料样品 :A1、A2、B1 和 B2。将切片分别如表 8 所示的那样进行处理。

[0093]　　　表 8

[0094]

坯料样品	处理 (坯料 -A)
A1	无
A2	HIP'ed:900℃ ;15ksi ;2 小时
B1	无
B2	HIP'ed:900℃ ;15ksi ;2 小时

[0095]　　　在热等静压压制处理之后,将样品 A2 和 B2 分别在切片的近似中心线处纵向切片,以产生用于扫描电子显微镜 (SEM) 的样品。样品 A1 和 B1 如接收时原样地被纵向切开,没有任何热等静压压制处理。按照 ASTM E1245-03(2008)-Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals by Automatic Image Analysis 测量连续的非金属夹杂物和孔隙空隙的最大尺寸和面积分率。使用 SEM 以背散射电子模式检查全纵向的横截面。对与每个切片样品而言,含有连续的非金属夹杂物和孔隙的三个最大可见区域的 SEM 场以 500 倍的放大倍率进行成像。图像分析软件用来测量在每个切片样品的三个 SEM 图像中的非金属夹杂物和孔隙的最大尺寸和面积分率。结果列于表 9。

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[0096]　　表 9

[0097]

样品	最大夹杂物尺寸 (微米)	最大面积分率 (%)	对应于最大夹杂物尺寸的 SEM 图像
A1	68.7	1.66	图 7A
A2	48.5	1.85	图 7B
B1	69.9	1.56	图 7C
B2	45.2	1.59	图 7D

[0098]　　结果表明,热等静压压制操作总体上降低了非金属夹杂物和孔隙的组合的尺寸和面积分率。图 7A 和图 7C 与图 7B 和图 7D 的比较,分别显示了热等静压压制操作减少了并在某些情况下消除了镍－钛合金坯料中的孔隙。

[0099]　　实施例 5:

[0100]　　镍－钛合金锭被热锻造、热轧和冷拉拔以产生 0.53 英寸直径的棒。将所述镍－钛合金棒热在 900℃和 15,000psi 下等静压压制 2 小时。将所述热等静压压制的棒纵向切片,以产生用于扫描电子显微镜 (SEM) 的五 (5) 个纵向样品切片。按照 ASTM E1245-03(2008)-Standard Practice for Determining the Inclusion or Second-Phase Constituent Content of Metals by Automatic Image Analysis 测量连续的非金属夹杂物和孔隙空隙的最大尺寸和面积分率。使用 SEM 以背散射电子模式检查全纵向的横截面。对与每个样品切片而言,含有连续的非金属夹杂物和孔隙的三个最大可见区域的 SEM 场以 500 倍的放大倍率进行成像。图像分析软件用来测量在每个样品切片的三个 SEM 图像中的非金属夹杂物和孔隙的最大尺寸和面积分率。结果列于表 10。

[0101]　　表 10

[0102]

样品切片	最大夹杂物尺寸 (微米)	最大面积分率 (%)	对应于最大夹杂物尺寸的 SEM 图像
1	36.8	1.78	图 8A
2	34.3	1.36	图 8B
3	37.1	1.21	图 8C
4	37.7	1.60	图 8D
5	45.0	1.69	图 8E
平均	38.2	1.53	----

[0103]　　结果表明,所述冷拉拔和热等静压压制的镍－钛合金棒总体上满足 ASTM F 2063-12 标准规则的要求 (39.0 微米 (0.0015 英寸) 的最大允许长度尺寸,以及最大面积分率 2.8%)。图 6A-6H 的研究表明,热等静压压制操作消除了镍－钛合金棒中的孔隙。

[0104]　　本说明书通过参考各种非限制性和非详尽实施方案编写。然而,本领域的普通技

术人员应认识到,可在本说明书的范围内对任何公开的实施方案（或其部分）作出各种替换、修改或组合。因此,应预期并理解,本说明书支持本文未明确阐述的其他实施方案。例如通过组合、修改或重新组织本说明书中描述的各种非限制性实施方案的任何公开步骤、组件、元素、特点、方面、特征、限制等可以获得这样的实施方案。以这种方式,申请人保留在执行过程中修订本权利要求书的权利,以添加本说明书中不同描述的特点,并且这样的修订符合 35U.S.C. §§112(a) 和 132(a)。

图 1

图 2B

加工
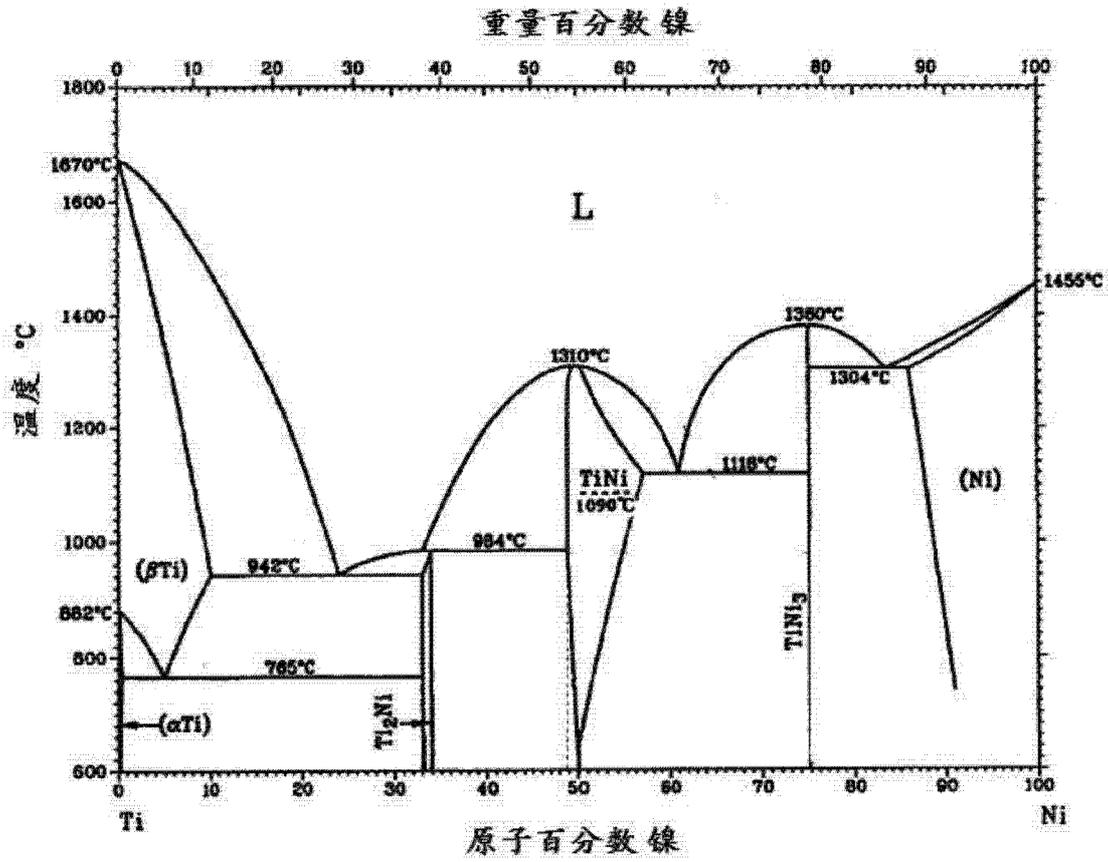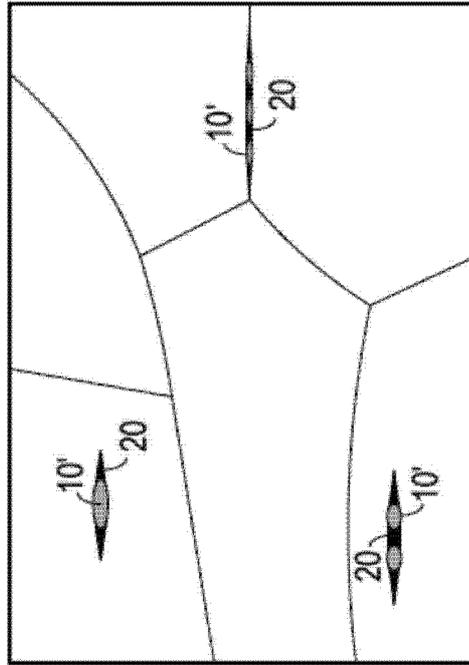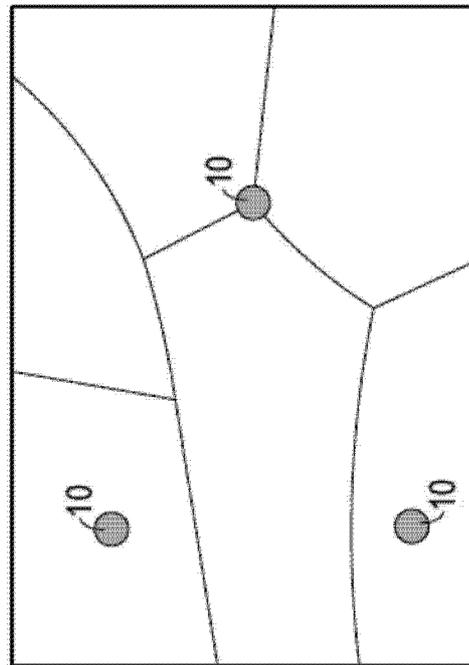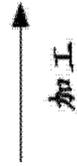
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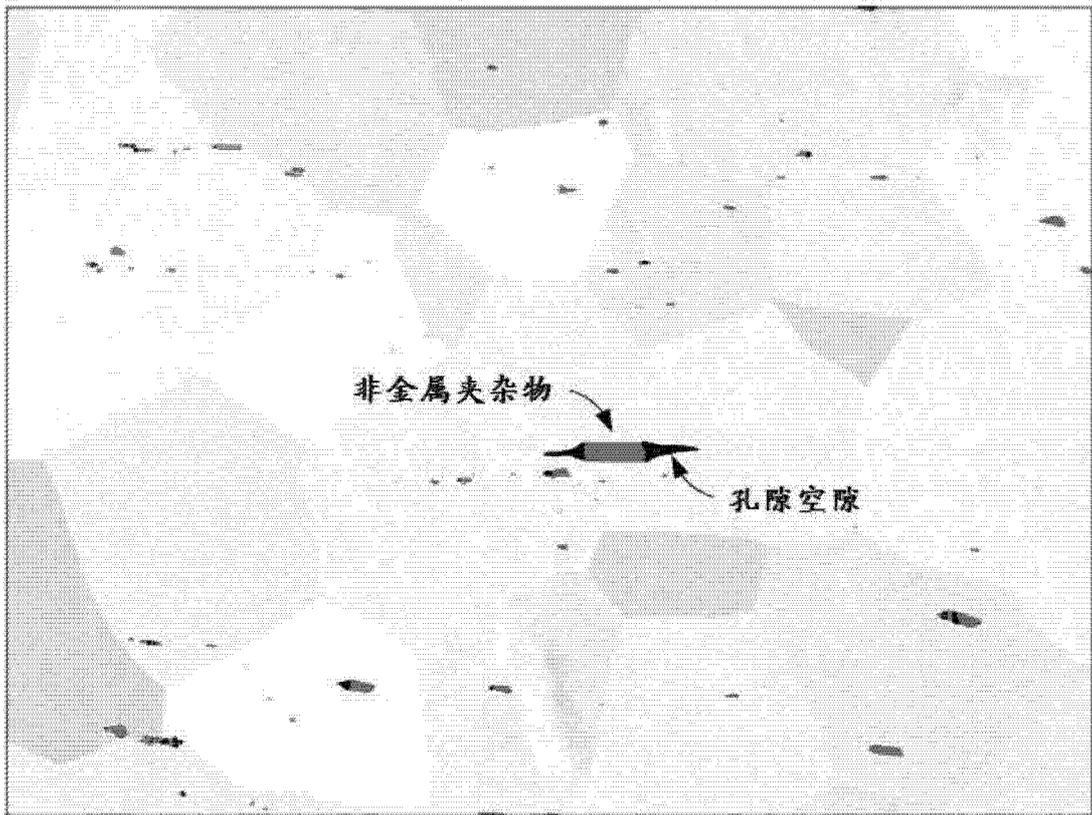
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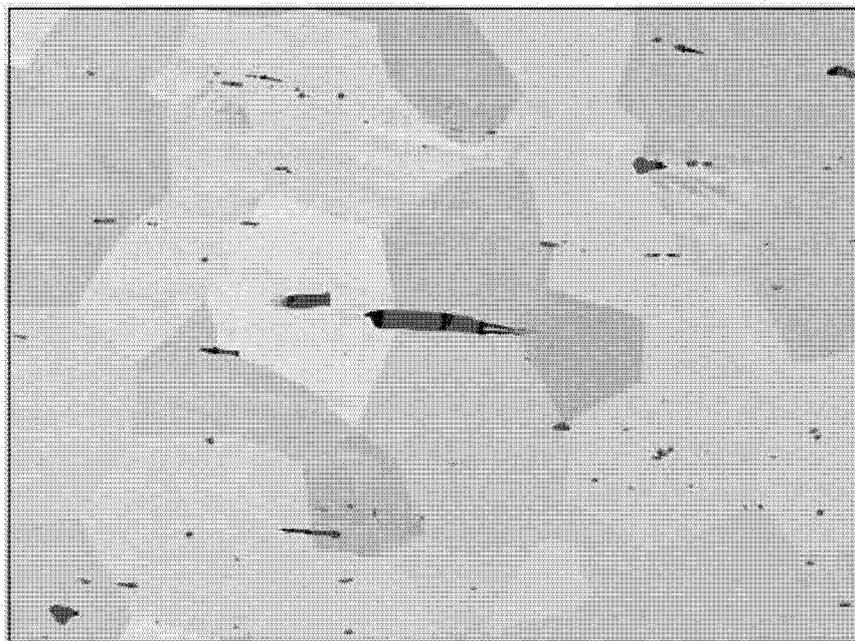
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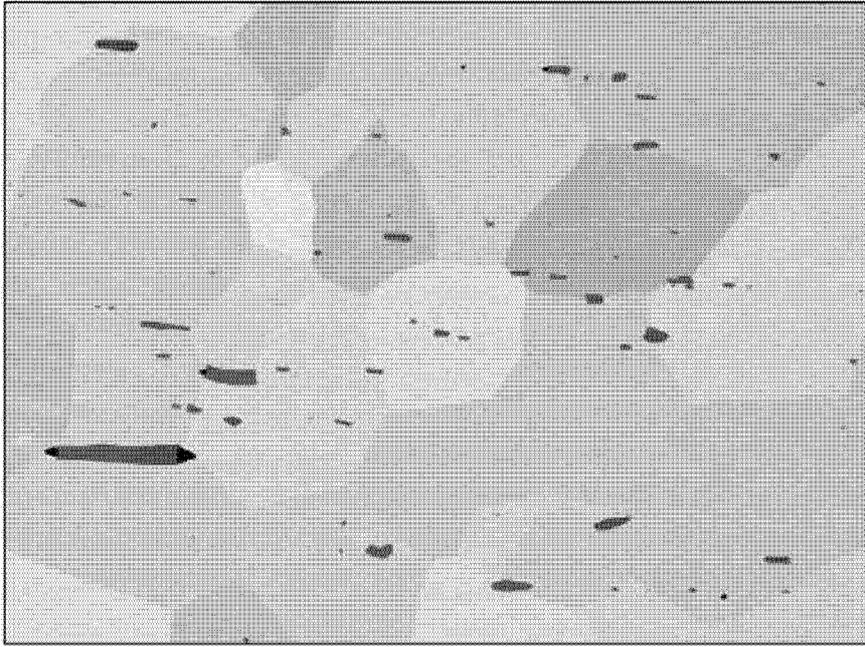
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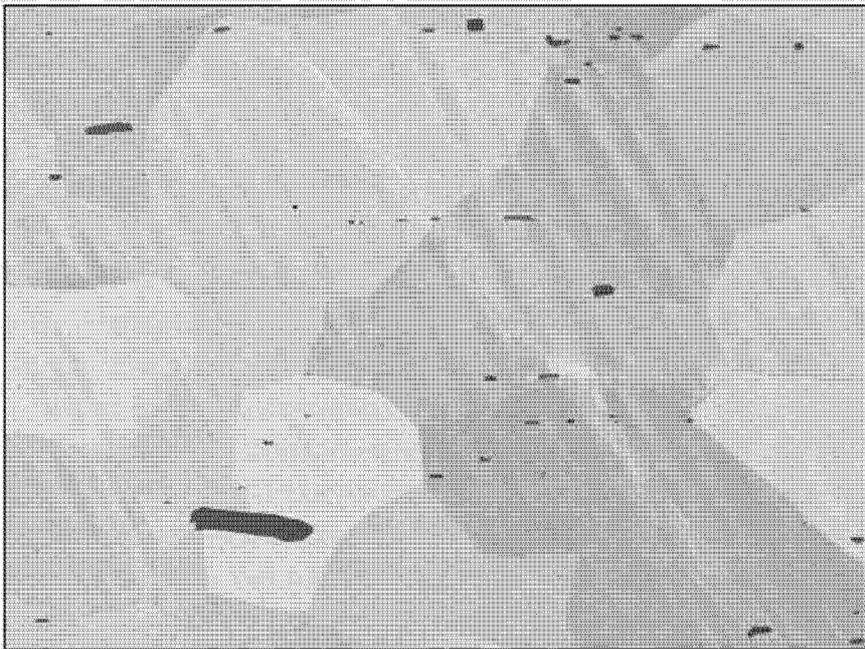
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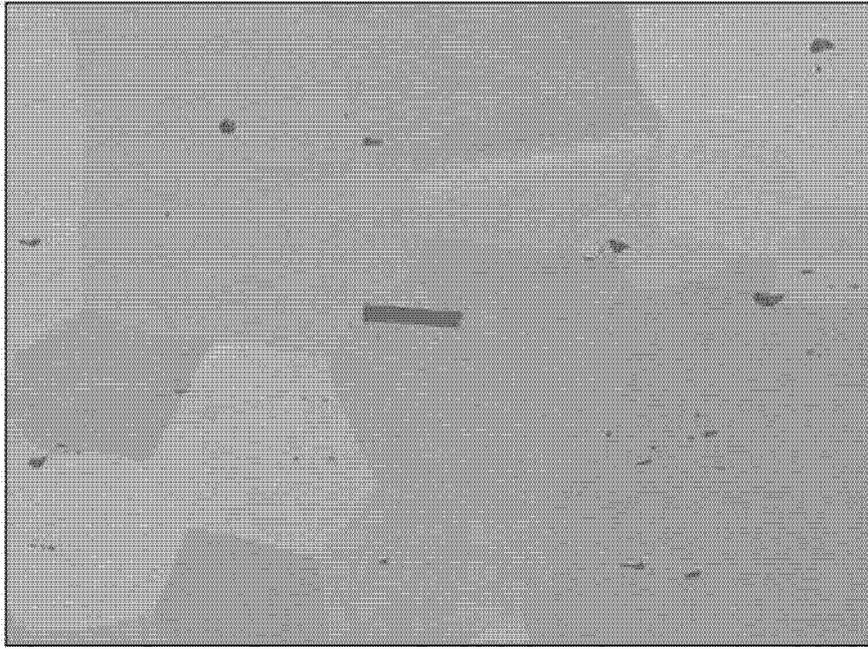
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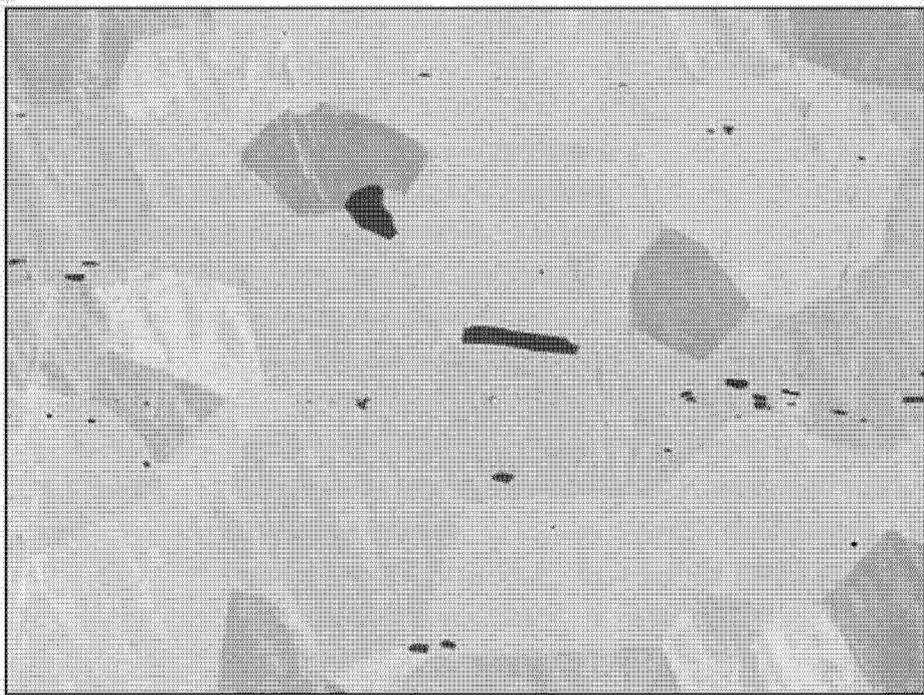
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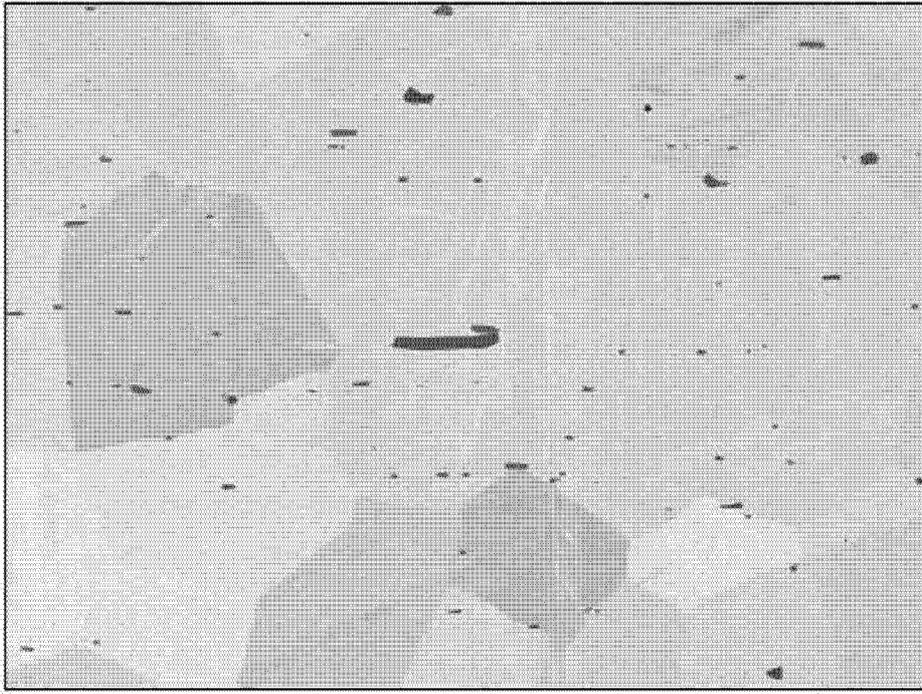
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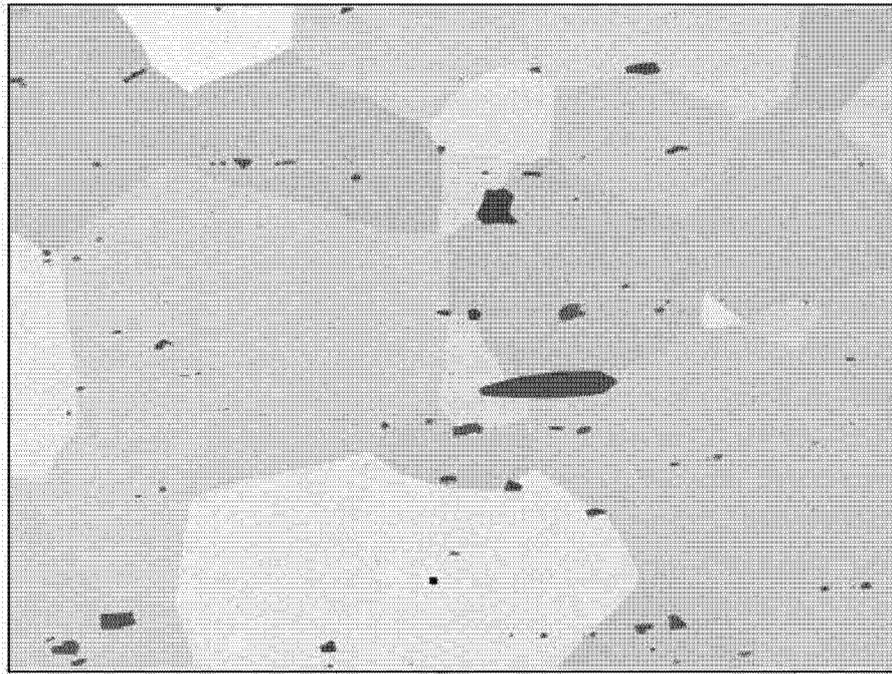
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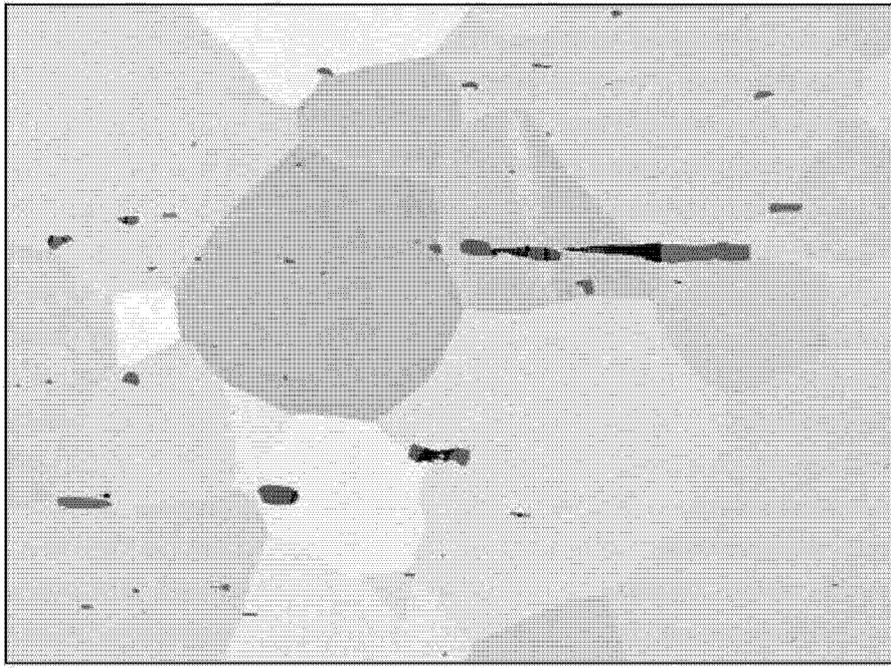
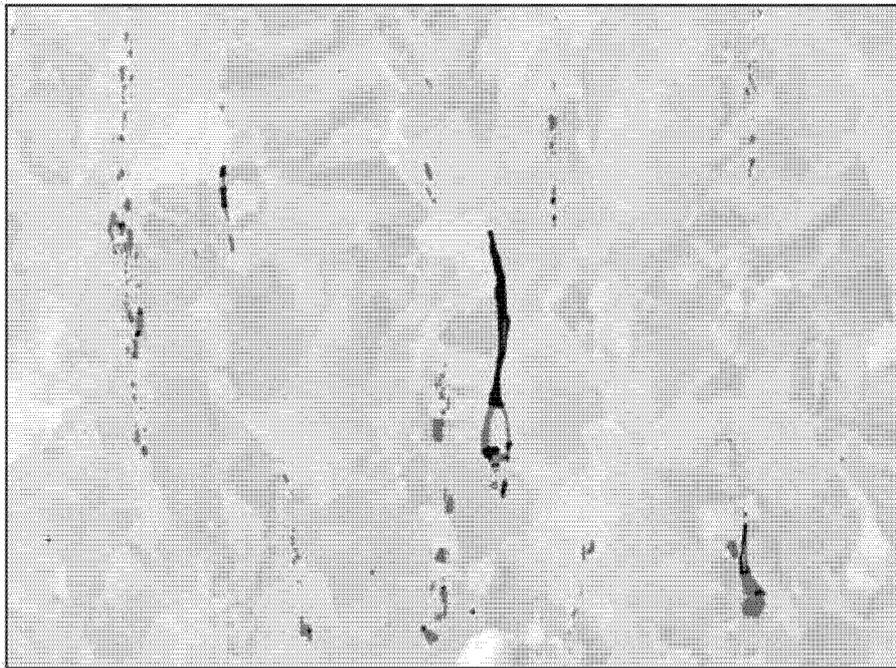图 5A
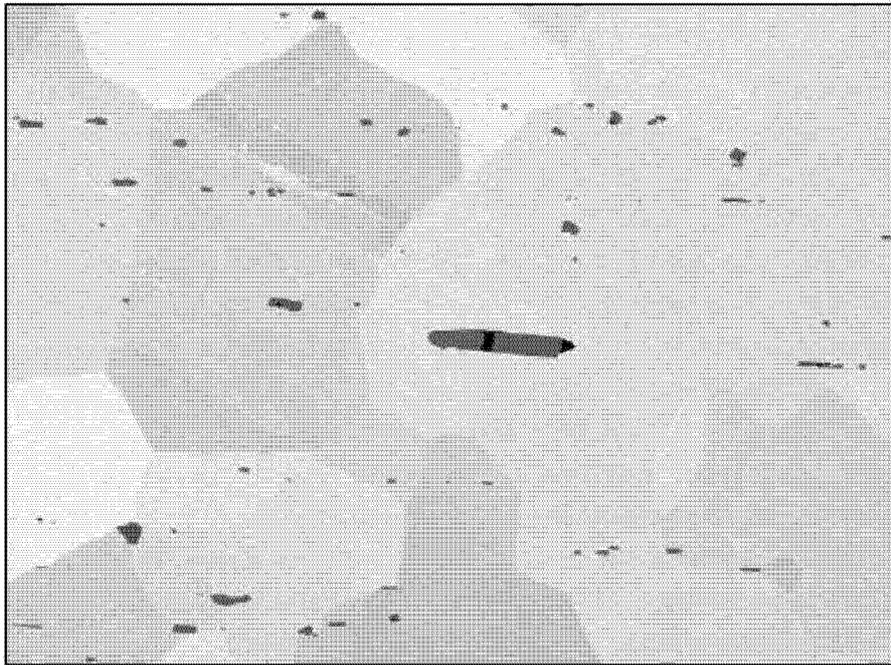
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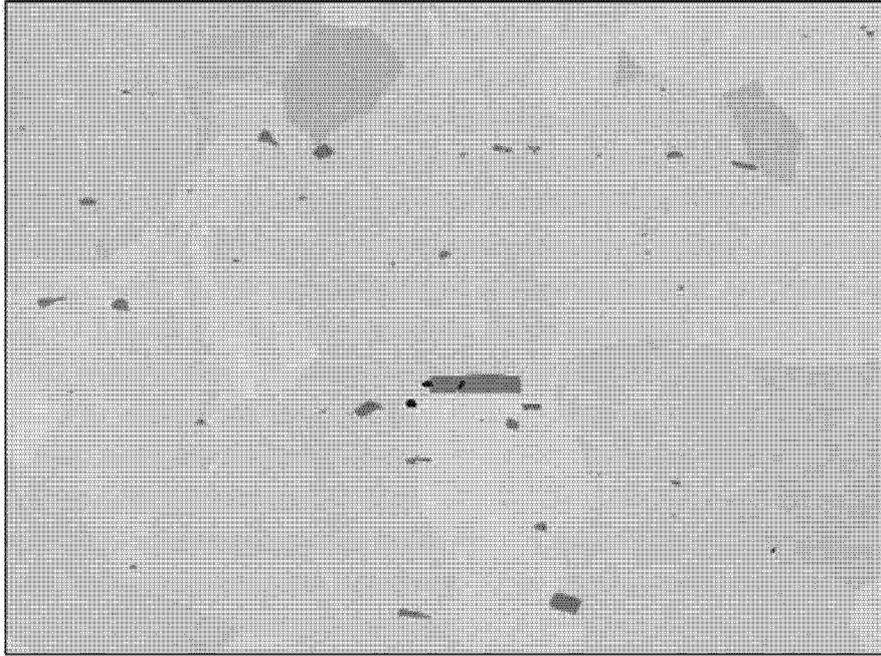
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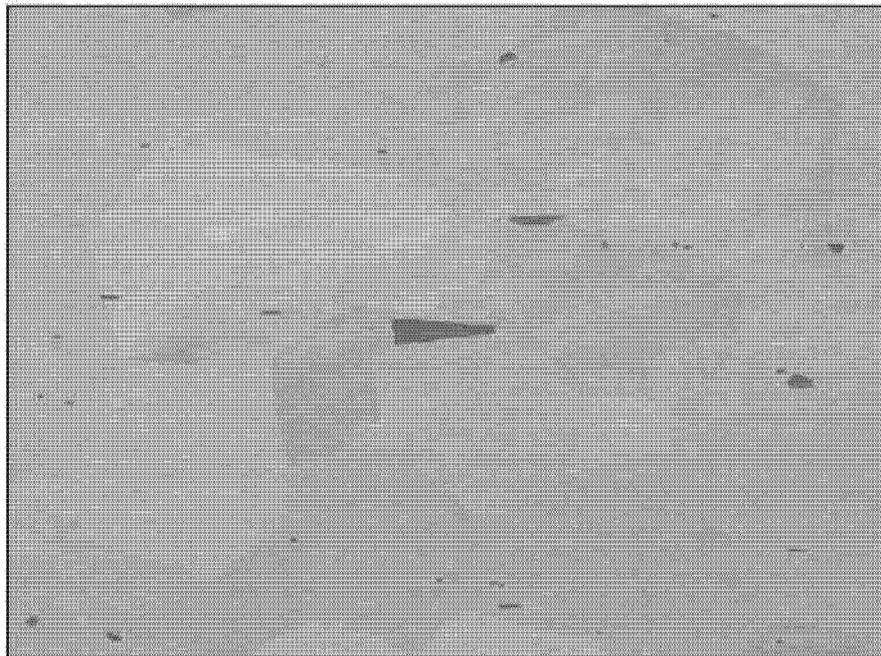
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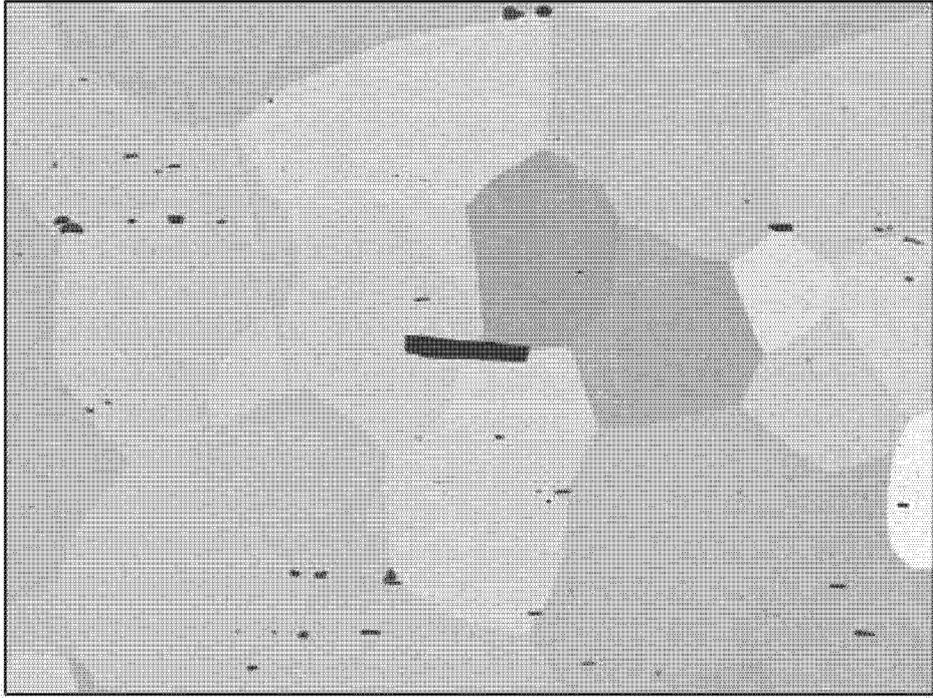
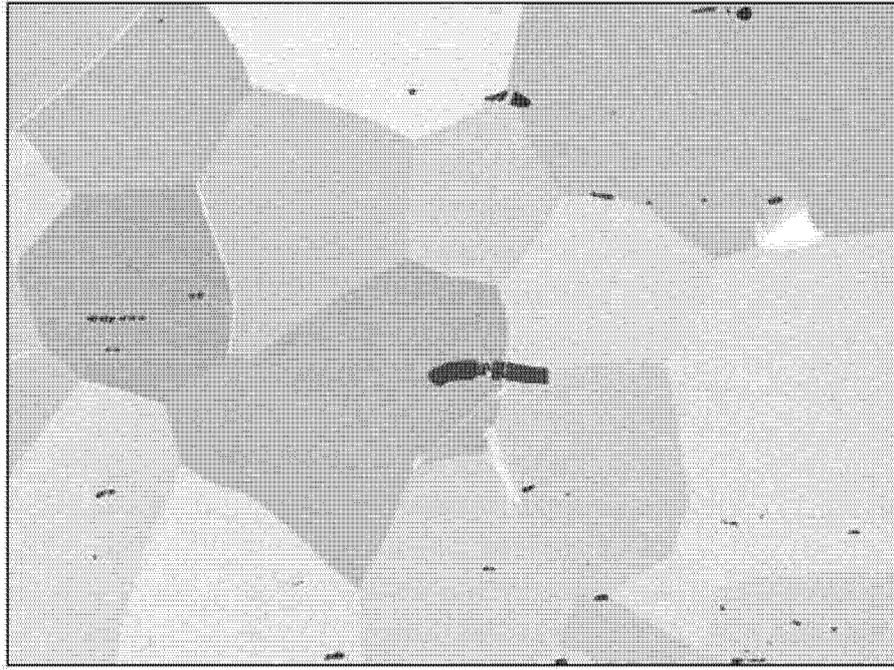图 5E
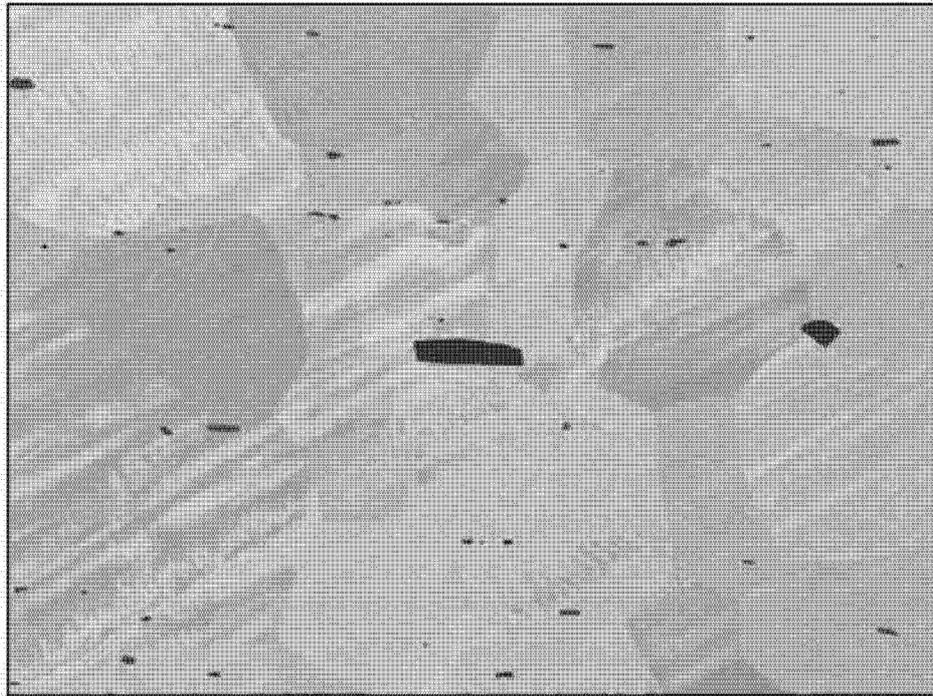
图 5F

图 5G
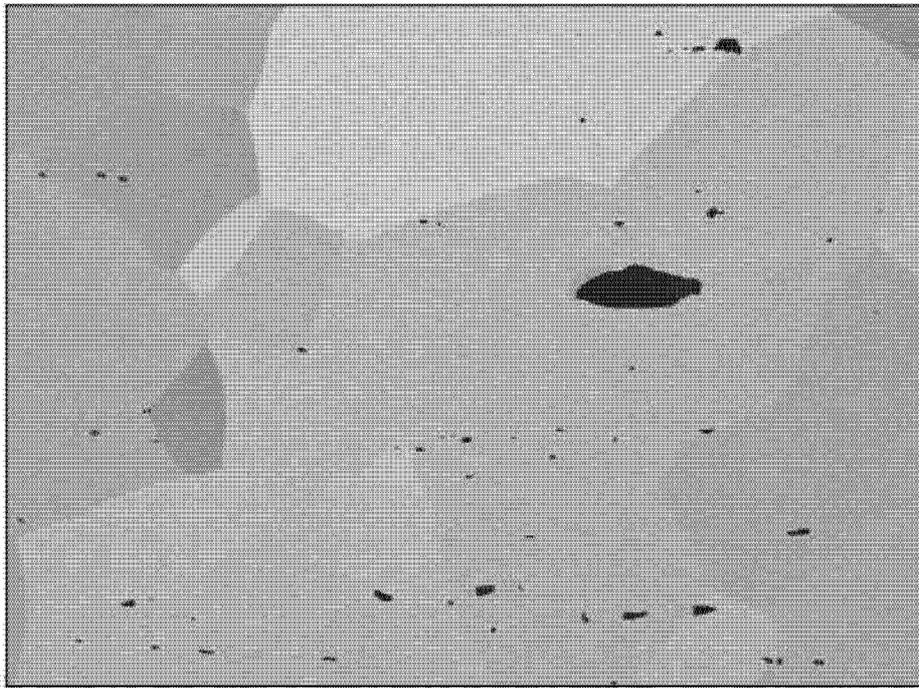
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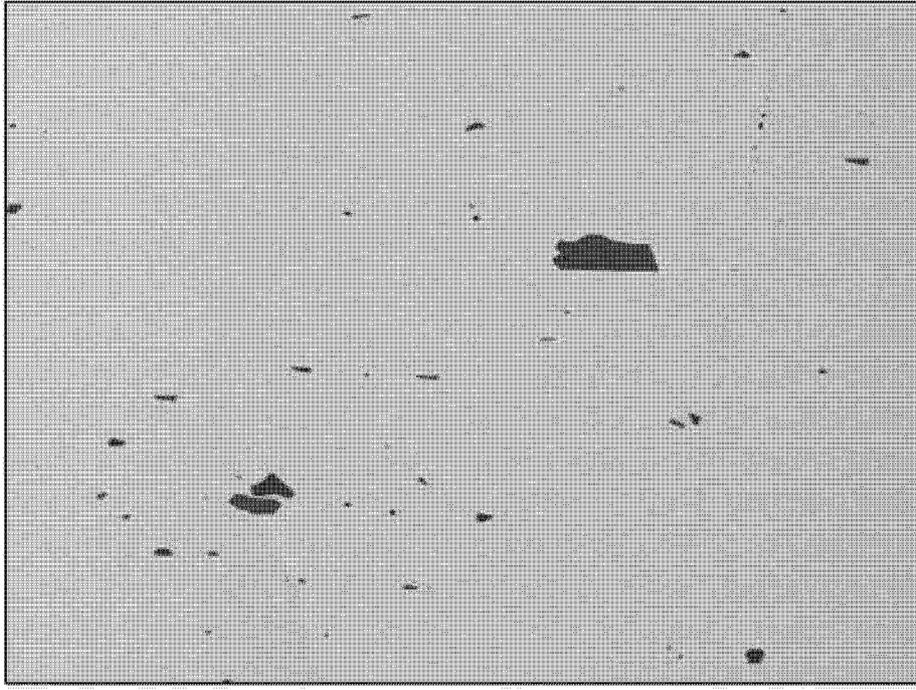
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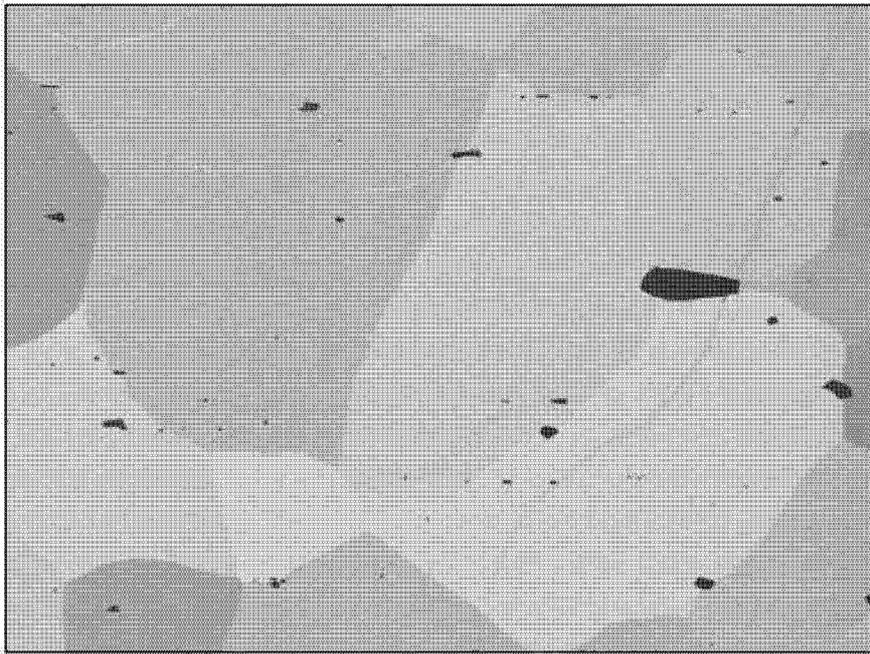
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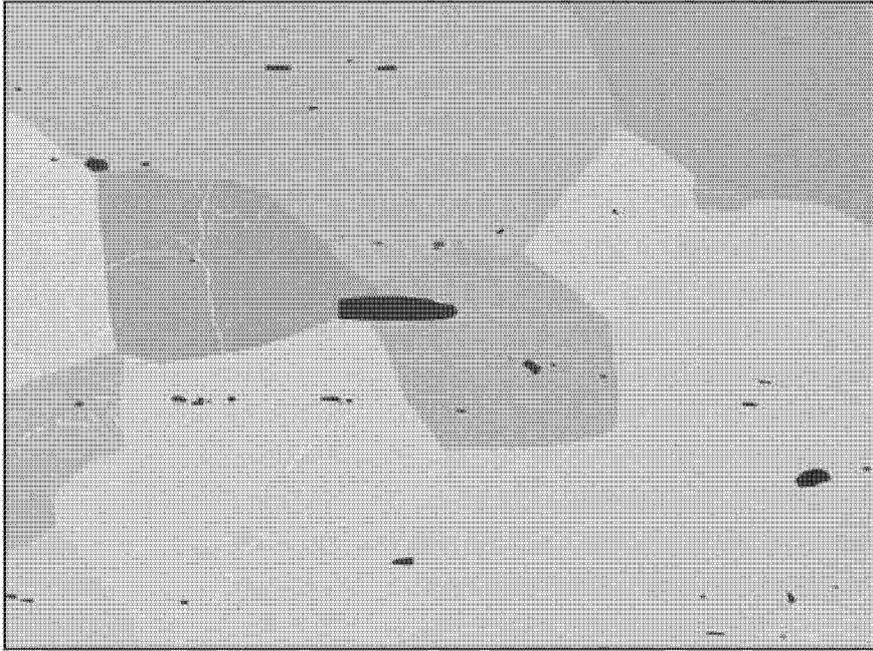
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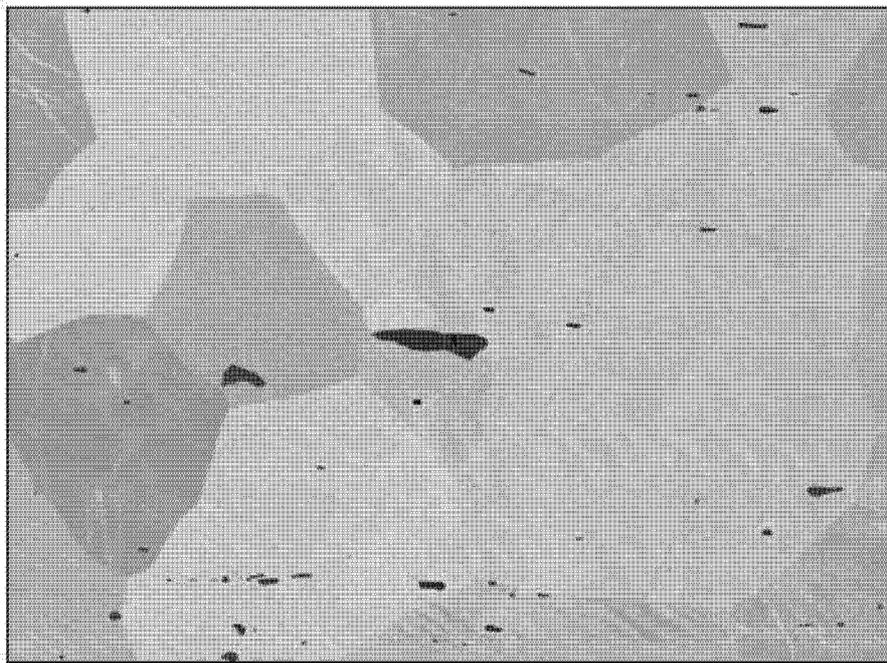
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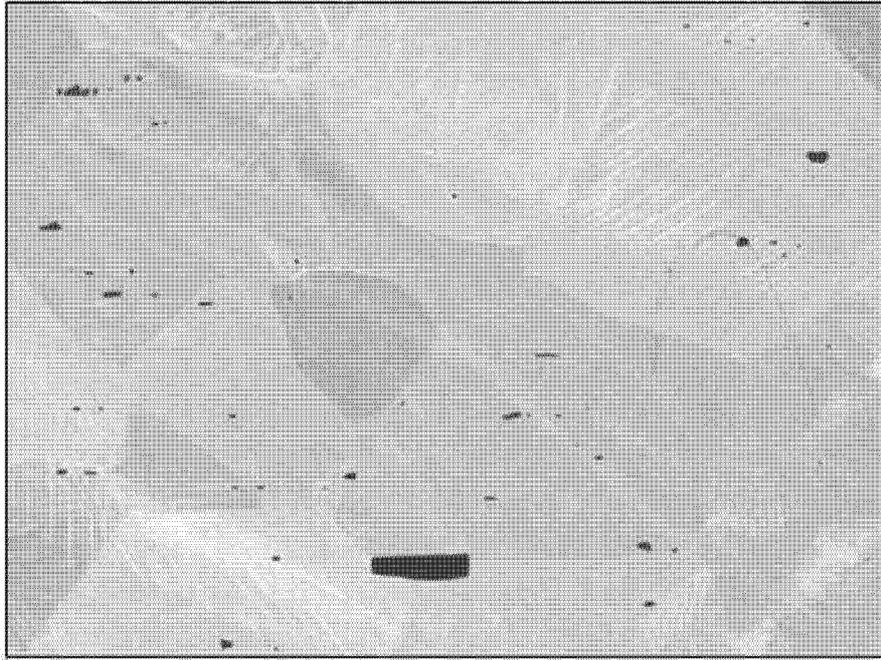
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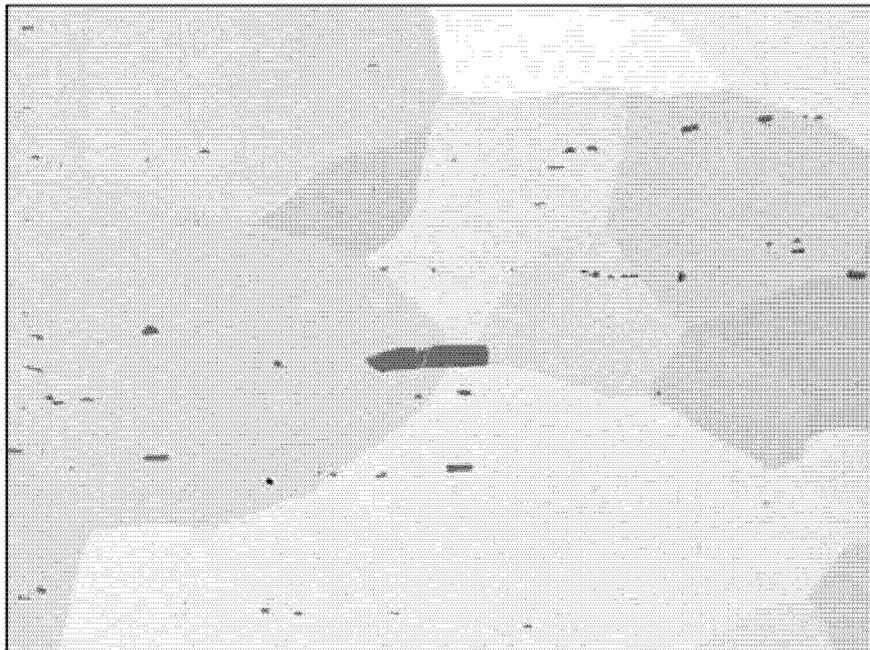
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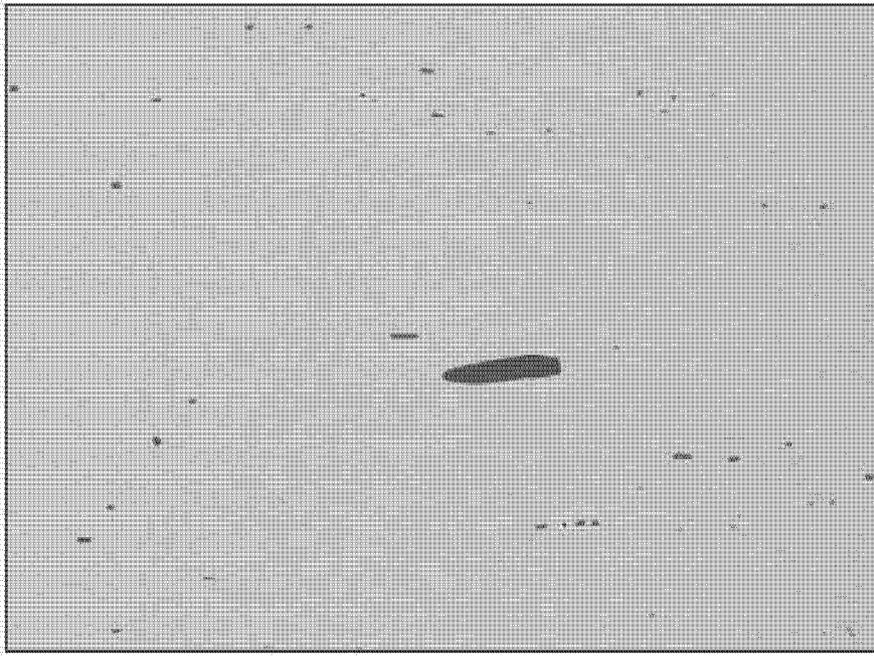
图 6H

图 7A

图 7B
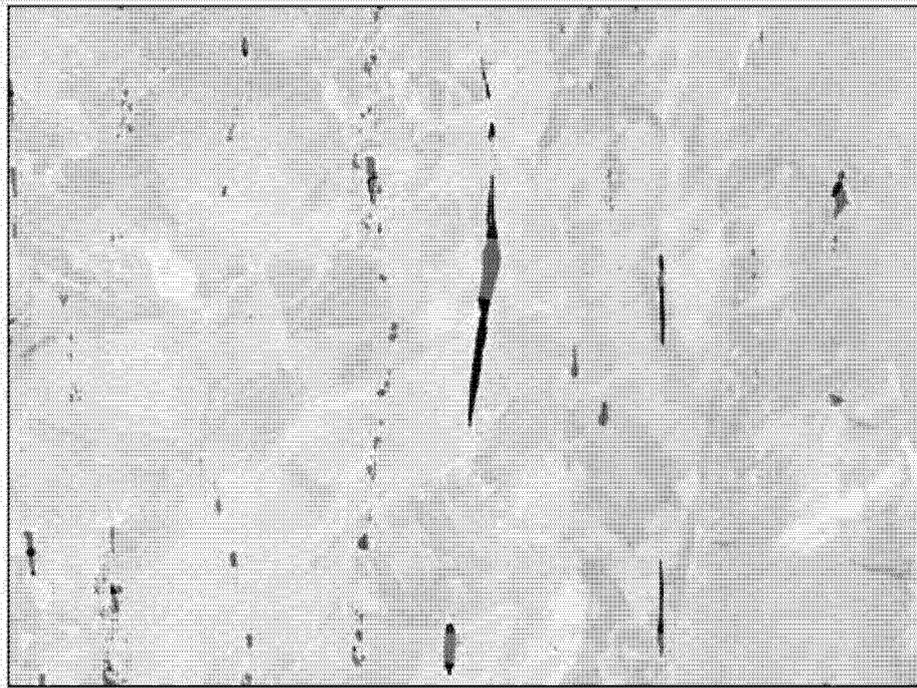
图 7C

图 7D

图 8A

图 8B

图 8C

图 8D

图 8E