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(54) **METHOD OF TREATING A WORKPIECE COMPRISING A TITANIUM METAL AND OBJECT**

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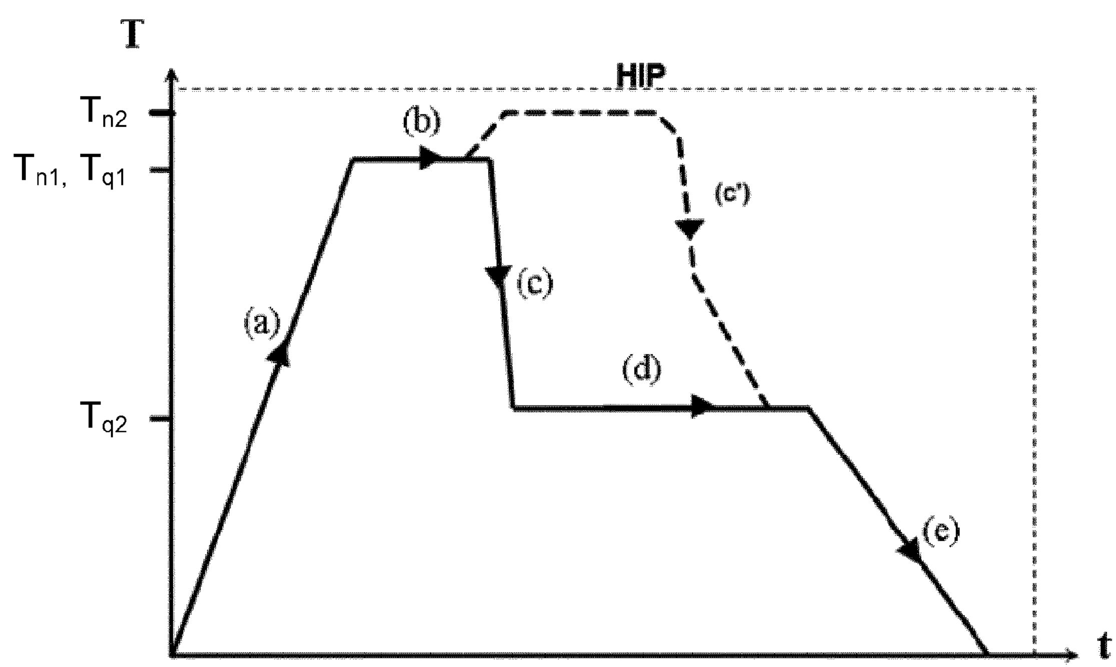
(57) **ABSTRACT**

Method of treating a workpiece comprising a titanium metal, wherein a titanium metal surface layer of the workpiece is converted to titanium nitrides. The method comprises the following steps; a) heating the workpiece to an initial nitriding temperature (T_{n1}) and b) subjecting said workpiece to one or more nitriding temperatures (T_{n1}, T_{n2}) for predetermined time(s) in a nitrogen containing gas under high pressure at hot isostatic pressing (HIP) conditions for converting the titanium metal surface layer to a first layer portion consisting of titanium nitrides and a second layer portion comprising a nitrogen gradient in the titanium metal. The method further comprises c) quenching the workpiece in the nitrogen containing gas under high pressure at hot isostatic pressing (HIP) conditions, in order to strengthen the titanium metal below the in step b) formed first nitride layer portion.



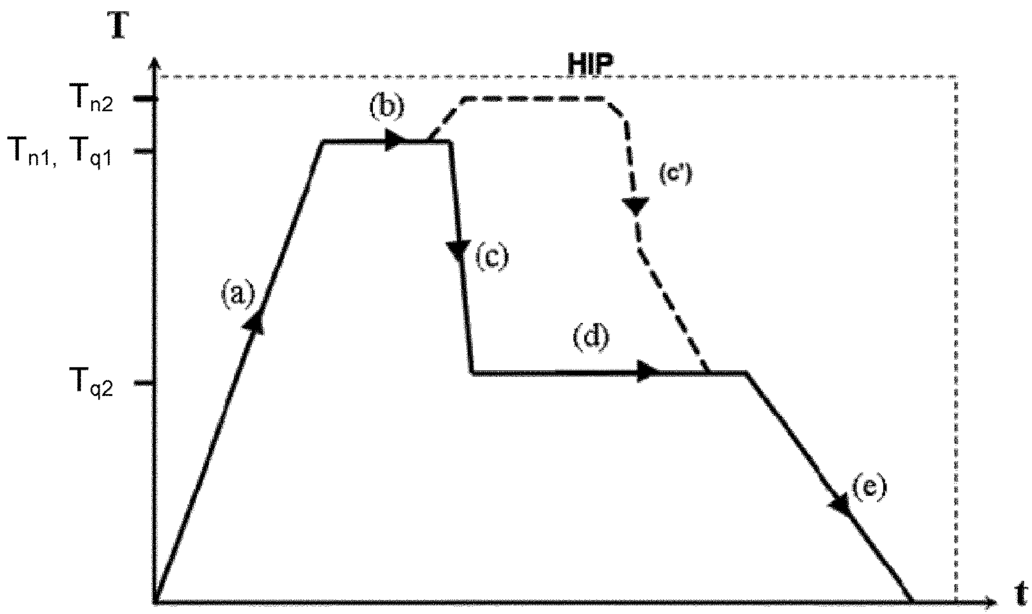


Fig. 1

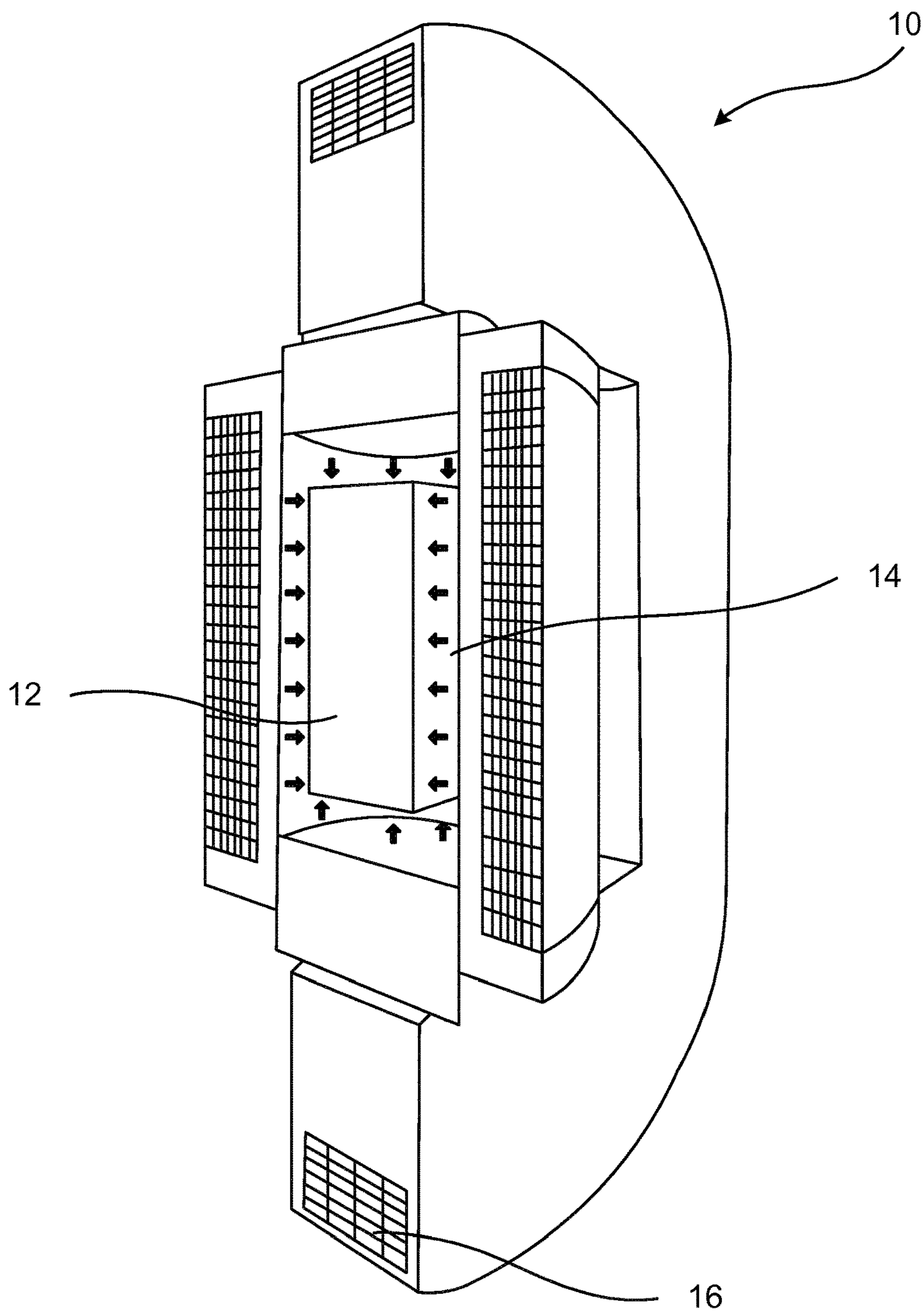


Fig. 2

METHOD OF TREATING A WORKPIECE COMPRISING A TITANIUM METAL AND OBJECT

TECHNICAL FIELD

[0001] The present invention generally concerns a method of treating a workpiece comprising titanium metal. More specifically it relates to a method which comprises nitriding at least a portion of the workpiece such that a surface layer of the titanium alloy is converted to titanium nitride. The invention also concerns an object, which has been subjected to such a method.

BACKGROUND OF THE INVENTION

[0002] Titanium has found an increasing use in various technical fields such as in the manufacturing of machine parts and other components within the automotive, aerospace, mining, medical and other industries. In practice, chemically pure titanium is not utilized industrially but the titanium is alloyed to form various alloys with differing characteristics. Examples of some frequently used titanium alloys are so called commercially pure (cp) titanium or Grade 2 titanium (sometimes referred to as unalloyed), Grade 5 titanium (Ti-6Al-4V) and Grade 9 titanium (Ti-3Al-2.5V). In the following description also the so called commercially pure titanium metal is referred to as alloy.

[0003] The titanium alloys generally have some characteristics that are favourable in many applications. Examples of such characteristics are low density, high specific strength or strength-to-weight ratio, excellent corrosion resistance and ability to withstand high temperatures. The low density and high specific strength e.g. contributes to reduce energy consumption and environmental impact when producing machine parts and other components. Some titanium alloys are also non-toxic which is used e.g. for producing orthopaedic and dental prosthesis and implants. However, one technical disadvantage of titanium alloys is the risk of adhesive seizure in highly loaded sliding or rolling contacts.

[0004] Several methods have been developed in order to eliminate this disadvantage. Such known methods comprise different PVD (Physical Vapour Deposition) coatings and plasma sprayed coatings.

[0005] An emerging method is conversion of the titanium alloy surface by nitriding the titanium alloy. By this means, ceramic titanium nitrides such as δ-TiN (face-centered cubic) and ε-Ti_2N (tetragonal) are formed in an outermost first surface layer portion of the work piece. The nitrides considerably increase the hardness and thereby the load-carrying capacity of the surface layer. In addition to forming nitrides in the outmost first ceramic layer portion, the nitriding process also results in a second metallic layer portion where nitrogen is diffused into the titanium alloy just beneath the ceramic layer. Typically the nitrogen concentration in this second layer portion is highest adjacent to the first nitride layer portion and is reduced gradually at increased depth from the surface, thereby forming a nitrogen gradient in the surface layer. The nitrogen gradient results in increased hardness and support of the first nitride layer portion.

[0006] This method is usually carried out by processing the workpiece in vacuum furnaces. The main limitations of these treatments are long and costly processes, resulting thin nitride layers and shallow penetration of nitrogen into the bulk metal, thereby forming merely a relatively weak support for the hard and brittle nitride layers.

PRIOR ART

[0007] The conference proceedings paper "The HIP-Nitriding of Steels and Ti-based Alloys" (M. H. Jacobs, M. A. Ashworth and A. J. Marshall; presented at the International Conference on Hot Isostatic Pressing, 20-22 May 1996 in Andover, Mass.) discloses a method for improving the productivity of the nitriding process by concurrently increasing both the thickness of ceramic nitride layers and the nitrogen penetration into the bulk metal, by subjecting the titanium parts to nitriding at very high nitrogen pressures for shorter durations by Hot Isostatic Pressing.

[0008] Hot Isostatic Pressing (HIP) is a process that is today mainly used to either eliminate the internal porosity of metal castings of titanium and nickel-based super-alloys or to densify various metallic and ceramic powder bodies to solid materials. The HIP process subjects a workpiece to concurrently elevated temperature and isostatic gas pressure (whereby pressure is applied to the material from all directions) in a high pressure containment vessel. An inert gas such as argon is usually used to prevent chemical reactions, and the pressurizing gas is usually raised to a pressure level between 100-200 MPa by a combination of pumping and electrical heating of the gas surrounding the work pieces. When materials are treated with HIP, the simultaneous application of heat and pressure eliminates internal porosity through a combination of plastic deformation, creep, and diffusion bonding.

[0009] U.S. Pat. No. 4,511,411 further discloses a method for increasing the surface hardness of a titanium alloy component. The method comprises; placing a component of titanium alloys in an autoclave, pumping nitrogen gas or ammonia into the autoclave and exposing the component in the autoclave for three hours to a pressure of 900 bar (90 MPa) and a temperature of 1 000° C.

SUMMARY OF THE INVENTION

[0010] An object of the present invention is to provide an enhanced method of treating a workpiece comprising a titanium metal alloy.

[0011] Another object is to provide such a method by which a surface layer of the titanium metal alloy workpiece is efficiently hardened by nitriding.

[0012] Yet another object is to provide such a method which allows for an enhanced control of the resulting material properties of the workpiece.

[0013] Still another object is to provide such a method by which the resulting microstructure of the workpiece may be efficiently and precisely controlled.

[0014] A further object is to provide such a method which may be carried out in an efficient, time saving manner at a comparatively low cost.

[0015] These and other objects are achieved by a method of the type specified in the preamble of claim **1**, which method comprises the special technical features defined in the characterizing portion of that claim.

[0016] The method is used for treating a workpiece comprising at least one titanium metal and involves that a titanium metal surface layer of the workpiece is converted to titanium nitrides. The method comprises the steps of; a) heating the workpiece to an initial nitriding temperature and;

b) subjecting said workpiece to one or more nitriding temperatures for predetermined time(s) in a nitrogen containing gas under high pressure at Hot Isostatic Pressing (HIP) conditions for converting the titanium metal surface layer to a first layer portion consisting of ceramic titanium nitrides and a second layer portion comprising a nitrogen gradient in the titanium metal. The method further comprises c) quenching the workpiece in the nitrogen containing gas under high pressure at Hot Isostatic Pressing (HIP) conditions as a first step in a hardening heat treatment, in order to further strengthen the titanium metal below the first ceramic nitride layer portion formed in step b).

[0017] The method according to the present invention improves the mechanical properties of the workpiece. The high nitrogen gas pressure enhances nitrogen diffusion from the gas into the titanium metal, resulting in conversion to nitrides in the first ceramic layer portion and creating a nitrogen gradient in the second titanium metal layer portion. Nitriding at HIP conditions thus results in thick ceramic δ-TiN and ε-Ti_2N surface layers and in a deep nitrogen gradient layer which additionally exhibits a high nitrogen content immediately below the nitride layer to improve its load-carrying capacity. According to the invention these favourable features is combined with an improved heat transfer by the highly pressurized gas during the quenching step. Quenching at HIP conditions not only increases the heat transfer but also promotes equal cooling of all surfaces regardless of their position and orientation on the workpieces and within the pressure vessel.

[0018] The prior art does not disclose a nitriding method of titanium alloys which subsequently comprises quenching under high isostatic pressure as a first step in a hardening heat treatment, using Hot Isostatic Pressing also for prior nitriding and concurrent elimination of casting porosity and/or residual stresses in the titanium alloys. The present invention is based on the realization that recent developments in HIP equipment makes it possible to utilize the improved heat transfer capability achieved by Hot Isostatic Pressing for quenching and thereby to carry out hardening heat treatments under HIP conditions.

[0019] Quenching the workpiece at isostatic pressures of up to 200 MPa in a gas such as nitrogen, which at these pressures has a viscosity resembling water, provides that the titanium metal comprising both the nitrogen gradient portion and the bulk titanium metal can be subjected to very high cooling rates (delta T/s). The excellent heat transfer capabilities at high isostatic pressures also provide that the cooling rate may be precisely controlled within wide intervals. By this means, the resulting material properties after quenching may be precisely controlled by varying and controlling the cooling rate at different stages of the quenching process. By quenching the workpiece under HIP conditions, the microstructures and resulting properties can be optimized for different applications. The quenching may e.g. be carried out such that the hardness and/or ductility of both the nitrogen gradient layer and the bulk metal is increased. The nitrogen gradient layer and the bulk metal may thus be formed to constitute an excellent support for the hard and brittle nitride layers at the surface. By this means the method may be utilized for producing workpieces and components which have excellent properties in regard of e.g. hardness, low friction, ductility, durability, specific strength, temperature resistance and low density.

[0020] If desired, the invention also allows for that the cooling rate is further increased by utilizing heat exchangers and fans within the pressure chamber in which the method according to the invention is carried out. This enables even larger cross-sections of a workpiece to be cooled at sufficient rates. Since the workpiece is within a firm isostatic grip, its macroscopic shape is still preserved, and such high cooling rates will therefore not result in large residual stresses, cracks or warpage.

[0021] The invention further allows for that both nitriding the surface layer and quenching the workpiece is carried out subsequently or even at least partly overlapping in a continuous method step. Irrespective of if the nitriding and quenching operations are carried out overlapping or subsequently, both processes may be carried out in one and the same HIP chamber, thereby eliminating any need for intermediate cooling, transportation, storing, reheating and other handling of the workpiece. The combined nitriding and quenching in a single HIP chamber further eliminates the need for separate chambers, ovens, furnaces and other equipment needed when conducting nitriding and quenching as separate operations.

[0022] The method according to the present invention therefore provides a cost-effective way of obtaining titanium nitride layers on titanium alloys, which in addition is heat treated for superior properties. Additionally, improved strength and ductility with reduced scatter may be obtained due to the elimination of all internal porosity in the cast work piece. Further, the method offers the possibility of manufacturing work pieces with closer machining tolerances since residual stresses are eliminated from the work piece, and batch-processing time may be decreased.

[0023] As the quenching step c) is carried out under HIP conditions, a rapid cooling, typically greater than or equal to 100 K/min is possible, exceeding the rate of quenching in oils, since the pressurized gas provides efficient heat transfer.

[0024] According to one embodiment the workpiece may, before step c), be subjected to at least one temperature at or above the β phase transus temperature for the titanium alloy in question for solution treatment of the titanium alloy to convert prior α phase or α+β phase structure to solely or predominantly β phase. Hereby, microstructures that are particularly favourable at some applications may be achieved after completing the method.

[0025] Step c) may comprise quenching the workpiece at a cooling rate which is high enough to, at least partly, transform β phase by a martensitic transformation directly to α' phase or α" phase. This also allows for achieving microstructures that give the workpiece properties which are desirable at various applications.

[0026] The quenching rate may be chosen to delay the remaining transformation of β phase to α phase at lower temperatures, resulting in substantially finer microstructures.

[0027] The workpiece may, after step c), be subjected to at least one aging temperature at a predetermined time to obtain precipitation hardening of the titanium alloy. When the workpiece comprises titanium Grade 5, it may e.g. be suitable to carry out the aging step at 400-600° C.

[0028] The workpiece may be cooled to room temperature after quenching or after subjecting the workpiece to the at least one aging temperature for a predetermined time.

[0029] The workpiece may be positioned in one and the same HIP chamber during the entire execution of the method. Hereby all intermediate transportation, storing other handling as well as cooling and re-heating of the workpiece is eliminated.

[0030] The workpiece may be subjected to the nitrogen containing gas under high pressure at Hot Isostatic Pressing (HIP) conditions during the entire execution of the method.

[0031] The titanium metal may preferably comprise at least one of the following; titanium alloy of Grade 1, Grade 2, Grade 5 or Grade 9. However, several other titanium alloys may also be treated by means of the method.

[0032] Step c) may be carried out at Hot Isostatic Pressure conditions where the nitrogen gas pressure is, at least initially, above to MPa. It may at some instances be suitable to reduce the gas pressure after quenching such that an excessive pressure does not counteract precipitation of particles with higher specific volume (i.e. lower density) during aging. However, the gas pressure should at all instances be maintained at least at or above 5 MPa for achieving sufficient heat transfer and thus temperature control.

[0033] The workpiece may comprise Grade 2 titanium and step c) may then comprise quenching the workpiece at a quenching rate of at least 900 K/min and preferably at least 1200 K/min.

[0034] The workpiece may alternatively comprise Grade 5 titanium and step c) may then comprise quenching the workpiece at a quenching rate of at least 210 K/min and preferably at least 420 K/min.

[0035] If the workpiece comprises Grade 9 titanium, step c) may comprise quenching the workpiece at a quenching rate of at least 300 K/min.

[0036] It should be noted that preferably all of the steps for nitriding, quenching, aging and cooling to room temperature may be carried out at least partly under HIP conditions in a single HIP chamber. Hereby, the entire treatment of the workpiece may be accomplished, without interruptions, in a single work station. By this means all intermediate handling between different works stations and operations is eliminated. It may also be noted that when also the cooling to room temperature of the workpiece is carried out in the HIP chamber, the high pressure may be maintained during the entire process. The temperature however, naturally needs to be decreased, such that this treatment step will not be carried out entirely at the high temperatures normally prevailing at HIP conditions. However, not all of the steps need necessarily be carried out under HIP conditions, as most benefits from HIP are gained during steps a) through c), while the aging treatment may take place in another furnace and the cooling to room temperature may be carried out in the aging furnace, another furnace or in the ambient surrounding.

[0037] The method thus allows for producing objects with extraordinary favourable properties and the invention also relates to such objects.

[0038] According to an aspect, the invention concerns an object comprising a titanium metal alloy of Grade 2, Grade 5 or Grade 9, which object exhibits a surface layer comprising a first nitride layer portion and second titanium metal portion with a nitrogen gradient, which surface layer extends to a depth of at least 50 μm when the titanium metal alloy is Grade 2 or Grade 9 and at least 75 μm when the titanium metal alloy is Grade 5.

[0039] The object may exhibit a hardness of at least 265 HV0,1 at 25 μm; at least 325 HV0,1 at 25 μm and at least 420 HV0,1 at 50 μm, when the titanium metal alloy is Grade 2, Grade 9 and Grade 5 respectively.

[0040] The titanium alloy of the object may exhibit solely or predominantly α' phase or α" phase structures.

[0041] The object may constitute or form part of a component chosen from a group of components comprising; automotive, aerospace, mining and medical components.

[0042] The workpiece thus comprises a nitrided titanium alloy having an improved combination of high strength, ductility and hardness. Such a workpiece is intended for use particularly, but not exclusively, in applications where high wear resistance is required or in applications in which strict specifications must be consistently met.

[0043] Generally, all terms used in the claims are to be interpreted according to their ordinary meaning in the technical field, unless explicitly defined otherwise herein. All references to "a/an/the element, apparatus, component, means, step, etc." are to be interpreted openly as referring to at least one instance of the element, apparatus, component, means, step, etc., unless explicitly stated otherwise. The steps of any method disclosed herein do not have to be performed in the exact order disclosed, unless explicitly stated.

BRIEF DESCRIPTION OF THE DRAWINGS

[0044] The invention is now described, by way of example, with reference to the accompanying drawings, in which:

[0045] FIG. **1** is a diagram representing temperature (T) and time (t) and schematically illustrating a method according to an embodiment of the invention.

[0046] FIG. **2** schematically illustrates a cross section in perspective view of a Hot Isostatic Press containing a work piece.

DETAILED DESCRIPTION OF EMBODIMENTS

[0047] The invention will now be described more fully hereinafter with reference to the accompanying drawings, in which certain embodiments of the invention are shown. This invention may, however, be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided by way of example so that this disclosure will be thorough and complete, and will fully convey the scope of the invention to those skilled in the art. Like numbers refer to like elements throughout the description.

[0048] FIG. **1** illustrates a nitriding heat treatment cycle according to an embodiment of the invention. A workpiece **12** consisting of or comprising at least one titanium alloy, such as Grade 2, Grade 5 or Grade 9, has been placed in a hot isostatic press **10** as shown by FIG. **2**. The workpiece may be, for example, engine parts such as wrist pins, hydraulic suspension parts, transmission parts, valves, pumps, orthopaedic or dental implants or prosthesis or the like.

[0049] The workpiece **12** is surrounded by a nitrogen containing gas **14** inside a chamber of the hot isostatic press **10**. In the shown example, the gas is nitrogen gas (N_2). It is however possible also to use other nitrogen-containing gases such as ammonium gas. During an initial phase of the treatment, the pressure of the gas **14** is increased, typically to a range between 100 and 200 MPa. The increase of the gas pressure may take place before, simultaneously with or after increasing the temperature in the gas **14**. Normally, the increase of the pressure and the temperature of the gas take place at least partly simultaneously.

[0050] As illustrated in FIG. **1**, the workpiece **12** is in step a) heated to an initial nitriding temperature (T_{n1}). The workpiece is thereafter subjected to this nitriding temperature T_{n1} for a first predetermined time. As indicated by the dashed line in FIG. **1**, the temperature may during the nitriding step b) be increased or decreased to any further nitriding temperature T_{n2} and kept at this temperature for any second predetermined time. The nitriding step b) may thus comprise subjecting the workpieces to any number of different nitriding temperatures for any respective desirable times.

[0051] During the nitriding step b), the titanium alloy surface layer is converted to titanium nitrides. Typically TiN is formed in the outermost layer and Ti_2N is formed further in from the outer surface. Additionally, nitrogen is diffused further into the titanium metal layer beneath the ceramic nitrides. In this metal layer portion the nitrogen content typically varies such that the nitrogen content is higher adjacent the nitrides and gradually decreases with increased material depth from the surface. I.e. the nitriding step b) results in the formation of a ceramic nitride layer portion and nitrogen gradient layer portion in the titanium metal.

[0052] At the example illustrated by solid lines in FIG. **1** the initial nitriding temperature T_{n1} lies above the β transus temperature of the titanium alloy in question. However, if nitriding is taking place at a nitriding temperature below the β transus temperature, it may be advantageous that the workpiece is heated above the (transus temperature to form the β structure of the titanium alloy in question, before quenching the workpiece.

[0053] In step c) the workpiece **12** is rapidly cooled during the quenching step of the method. During the quenching step c) the temperature of the workpiece **12** is decreased from an initial quenching temperature T_{q1} to a final quenching temperature T_{q2}. Normally, the initial quenching temperature T_{q2} is equal to the last nitriding temperature (T_{n1} in the example shown by solid lines in FIG. **1**). As indicated by the solid line c in FIG. **1**, the quenching may be carried out under an essentially constant cooling rate throughout the quenching step. However, it may be advantageous to vary the cooling rate such that the temperature decrease per second is different during the passages of different temperature intervals during the quenching process. Such a varying quenching is indicated by the dashed line c' in FIG. **1**.

[0054] By this means it is possible to control the grain size and formation of different phase structures of the titanium alloy. It should be noted that the quenching process primarily influences the properties of the titanium metal including the nitrogen gradient layer portion below the nitride layers in the work piece. By this means the quenching step of the method may be favourably used for controlling the material properties of the entire workpiece.

[0055] An important aspect of the invention is that the quenching step is carried out under hot isostatic pressing conditions. The high isostatic pressures prevailing in the chamber greatly contributes to an enhanced heat transfer between the surrounding gas and the workpiece. By this means, not only is it possible to achieve very high actual cooling rates of the material in the workpiece but it also allows for that the actual cooling rates of the material in the workpiece is accurately and precisely controlled throughout the quenching process.

[0056] It should also be noted that, while not illustrated in the figures, the efficiency of the quenching process may be further enhanced by introducing heat exchangers, fans and other heat transfer enhancing means in the chamber.

[0057] In the shown example, where the nitriding has taken place above the β transus temperature and the titanium alloy of the workpiece has been fully transformed to the β structure, it is in step c) quenched at a quenching rate of 150 K/min or higher under maintained HIP conditions.

[0058] In the shown example the quenching step c) is followed by an aging step d). At this step d), the workpiece is held at and aging temperature for a predetermined time. As seen in FIG. **1**, at this example, the aging temperature is equal to the final quenching temperature T_{q2}. However, it is also possible that the aging of the material of the workpiece is carried out at any other suitable temperature. Further, in the shown example, the aging step d) is carried out immediately subsequent to finalizing the quenching and under high isostatic pressure in the chamber of the hot isostatic press **10**.

[0059] At alternative embodiments of the invention, aging may be carried out at any pressure including atmospheric pressure inside or outside the hot isostatic press, e.g. in a conventional furnace. At some embodiments the aging step may even be fully dispensed with.

[0060] In step e), the workpiece is cooled to room temperature. Just as with the aging step d) cooling may take place under high pressure in the hot isostatic press **10** or under lower, such as atmospheric, pressure in the same press **10**. Alternatively, the cooling step may be carried out outside of the hot isostatic press **10**.

[0061] The workpiece may then be directly used in any application in which it is likely to be subjected to stress, strain, impact and/or wear under operation.

[0062] Furthermore, the workpiece may be machined, either before the heating step a) or after the nitriding, quenching and aging is completed, for example, if some particular surface treatment is required.

[0063] Carrying out the heating and nitriding step a) under HIP conditions accelerates the heating rate, nitriding rate and deep diffusion of nitrogen into the bulk titanium alloy. Carrying out the quenching step c) under HIP conditions accelerates the cooling rate and concurrently reduces residual stresses due to superplastic conditions during a substantial part of the quenching process.

[0064] Utilizing HIP conditions during any of the steps a) to d) and particularly steps a), b) and c) also results in the following advantages: elimination of casting porosity, elimination of residual stresses, consistent material properties and consistent machining properties.

[0065] FIG. **2** shows a hot isostatic press **10** in which one workpiece **12** is subjected to a method according to the embodiment of the invention illustrated in FIG. **1**. It should be noted that one or more workpieces may be placed inside the hot isostatic press **10** and that the work piece(s) can be of any shape and size as long as it/they can fit inside the hot isostatic press **10**. The workpiece **12** is radially and axially outwardly surrounded firstly by a pressurized gas **14** acting normally at all surfaces, secondly by furnace walls, thirdly by a heat insulating mantle and fourthly by the water-cooled pressure vessel walls, being held in compression by pre-stressed wire windings **16**.

[0066] All of the surfaces of the workpiece **12** as well as all of the surfaces of the furnace and the heat insulating mantle and the internal surfaces of the pressure vessel may be subjected to high-pressure nitrogen gas **14**, such as nitrogen at a pressure of up to approx. 200 MPa.

Example

[0067] Work pieces comprising commercially pure titanium (Grade 2) in the form of thin-walled tubes (t=1.0 mm) were placed in a hot isostatic press of the type illustrated in FIG. **2**. Nitrogen gas, N_2 was supplied to the chamber of the press **10**.

[0068] During step a) the temperature of the gas was increased until the temperature of the workpiece reached 960° C. Simultaneously, the pressure of the gas was increased to 170 MPa.

[0069] In step b) the same temperature and gas pressure was maintained for 2 hours.

[0070] Since this temperature was already above the "β transus" temperature, an increase in temperature in step b) was not needed for this titanium alloy.

[0071] In step c), the workpiece was quenched by cooling nitrogen gas according to the following cooling rates of the gas:

[0072] 3600 K/min between 960-900° C.,

[0073] 2460 K/min between 900-800° C.,

[0074] 1440 K/min between 800-700° C.,

[0075] 1020 K/min between 700-600° C. and

[0076] 600 K/min between 600-500° C.,

[0077] The temperature of the gas was measured by thermocouples.

[0078] In this case, no aging treatment was carried out.

[0079] In step e) the work pieces were cooled to room temperature.

[0080] All of the steps a), b) and c) were carried out in the hot isostatic press under nitrogen gas at pressures up to 170 MPa.

[0081] The thin-walled tubes were then analysed by microstructural determination and it was found that the material comprised a Widmannstätten structure with non-continuous β-phase. The microstructural analyse further determined the material of thin-walled tubes to have been cooled at >1200 K/min (>20 K/s) through the 888-868° C. interval for α+β structure formation at this cooling rate, corresponding to a water quench (WQ) rate. Since the cooling rate of the nitrogen gas was more than twice as high through at this temperature interval and since the heat transfer coefficient (>1000 $W/m^2 \times K$) is high between the dense gas and the thin-walled titanium tube, it is reasonable that the metal core could indeed be cooled by 20 K/s.

[0082] Microstructural evaluation further showed a formation of a 20 μm layer of δ-TiN+ε-Ti_2N with hardness up to 1068±22 HV0.05 at 1 μm depth and 519 HV0.025 at 10 μm depth, followed by a sloping decrease in hardness 30 μm further into the titanium metal to the bulk level of 230-250 HV0.1.

[0083] The invention has mainly been described above with reference to a few embodiments. However, as is readily appreciated by a person skilled in the art, other embodiments than the ones disclosed above are equally possible within the scope of the invention, as defined by the appended patent claims.

1. A method of treating a workpiece comprising a titanium metal, wherein a titanium metal surface layer of the workpiece is converted to titanium nitrides, which method comprises the following steps;

a) heating the workpiece to an initial nitriding temperature (T_{n1});

b) subjecting said workpiece to one or more nitriding temperatures (T_{n1}, T_{n2}) for predetermined time(s) in a nitrogen containing gas under high pressure at hot isostatic pressing (HIP) conditions for converting the titanium metal surface layer to a first layer portion consisting of titanium nitrides and a second layer portion comprising a nitrogen gradient in the titanium metal;

the method being characterized by;

c) quenching the workpiece in the nitrogen containing gas under high pressure at hot isostatic pressing (HIP) conditions at a quenching rate of at least 150 K/min, in order to strengthen the titanium metal below the, in step b) formed, first nitride layer portion.

2. The method according to claim **1**, wherein the work piece, before step c), is subjected to at least one temperature (T_{n1}) at or above the β phase transus temperature for the titanium alloy in question for solution treatment of the titanium alloy, to convert prior α phase or α+β phase structure to solely or predominantly β phase structure.

3. The method according to claim **1**, wherein step c) comprises quenching the workpiece at a cooling rate which is high enough to, at least partially, transform β phase by a martensitic transformation directly to α' phase or α" phase.

4. The method according to claim **1**, wherein said quenching rate is chosen for delaying the remaining transformation of β phase to α phase at lower temperatures, resulting in substantially finer microstructures.

5. The method according to claim **1**, wherein the workpiece, after step c), is subjected to at least one aging temperature (T_{q2}) at a predetermined time to obtain precipitation hardening of the titanium metal.

6. The method according to claim **1**, wherein the workpiece is cooled to room temperature after quenching or after subjecting the workpiece to the at least one aging temperature for the predetermined time.

7. The method according to claim **1**, wherein the workpiece is positioned in one and the same hot isostatic press chamber during the entire execution of the method.

8. The method according to claim **1**, wherein the workpiece is subjected to the nitrogen containing gas under high pressure at hot isostatic pressing (HIP) conditions during the entire execution of the method.

9. The method according to claim **1**, wherein the titanium metal comprises at least one of the following; titanium alloy of Grade 1, Grade 2, Grade 5 or Grade 9.

10. The method according to claim **1**, wherein said workpiece, in step b), is quenched at a quenching rate sufficient to prevent the formation of α phase structure.

11. (canceled)

12. The method according to claim **1**, wherein step c) is carried out at hot isostatic pressure conditions where the nitrogen gas pressure is at least initially above 10 MPa.

13. The method according to claim **1**, wherein the workpiece comprises titanium alloy of Grade 2, Grade 5 or Grade 9 and wherein step b) comprises quenching the workpiece at a quenching rate of;

at least 900 K/min and preferably at least 1200 K/min for Grade 2;

at least 210 K/min and preferably at least 420 K/min for Grade 5; or

at least 300 K/min for Grade 9.

14. An object comprising a titanium metal alloy of Grade 2, Grade 5 or Grade 9, characterized in that the object exhibits a surface layer comprising a first nitride layer portion and second titanium metal portion which exhibits solely or predominantly α' phase or α'' phase structures and a nitrogen gradient, which surface layer extends to a depth of at least 50 μm when the titanium metal alloy is Grade 2 or Grade 9 and at least 75 μm when the titanium metal alloy is Grade 5.

15. The object according to claim **14**, wherein the object exhibits a hardness of at least 265 HV0,1 at 25 μm; at least 325 HV0,1 at 25 μm and at least 420 HV0,1 at 50 μm, when the titanium metal alloy is Grade 2, Grade 9 and Grade 5 respectively.

16. (canceled)

17. The object according to claim **14**, which object constitutes or forms part of a component chosen from a group of components comprising; automotive, aerospace, mining and medical components.

18. The object according to claim **14**, which object has been subjected to a method according to claim **1**.

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