



Process for obtaining a fine-grained martensitic structure component

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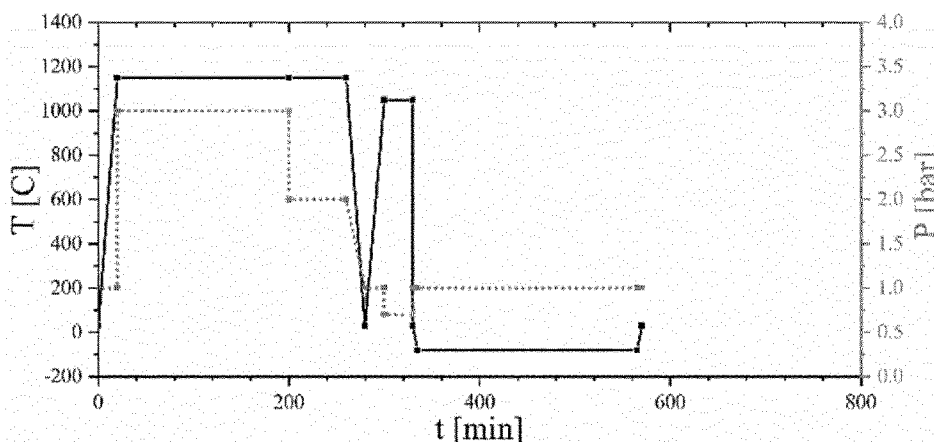


Fig. 1a

(57) **Abstract:** The disclosure relates to a process for the manufacture of a steel component comprising a fine-grained martensite structure component. The process comprises the steps of providing a steel component having an initial steel composition; introducing nitrogen into the steel component at a temperature T1 above 950°C, thereby creating an at least partly austenitic nitrogen-containing steel component; bringing the at least partly austenitic nitrogen-containing steel component to a temperature T2, such that austenite is decomposed into a steel component comprising at least an amount of carbon- and/or nitrogen-containing precipitates; bringing the steel component comprising at least an amount of carbon- and/or nitrogen-containing precipitates to a temperature T3 which is above T2, thereby creating an at least partly austenitic nitrogen-containing steel component optionally comprising at least an amount of carbon- and/or nitrogen-containing precipitates; and bringing the at least partly austenitic nitrogen-containing steel component to a temperature T4 that is below a martensite start temperature of the at least partly austenitic nitrogen-containing steel component for initiating transformation of at least some of the austenite into fine-grained martensite, thereby producing a steel component comprising a fine-grained martensite structure component.

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Process for obtaining a fine-grained martensitic structure component

Field of invention

The present disclosure relates to a process for the manufacture of a steel component comprising a fine-grained martensite structure component. The present disclosure
5 further relates to a steel component and use of a steel component comprising a fine-grained martensite structure component.

Background

Stainless steels are subdivided after their crystal structure at room temperature in ferritic, austenitic, duplex austenitic-ferritic and martensitic. Martensitic steel is initially
10 austenitic at high temperature and upon cooling, austenite transforms into martensite. High strength is a key feature of martensitic steel and is one of the fundamental characteristics making martensitic steel the material of choice for structural components, such as bearings, shafts and tools.

15 Martensitic stainless steels can be characterised as high- or low-carbon steels and may further comprise chromium and/or nitrogen. Generally, nitrogen is an interstitial alloying element of iron that can be used as a substitute or supplement for carbon. When compared to carbon, nitrogen can provide superior mechanical properties and corrosion resistance. However, because nitrogen has a low solubility in molten iron, it is
20 challenging to produce martensitic steels with a significant nitrogen content, for example greater than 0.1% by weight.

Martensitic steels with a nitrogen content may be produced by pressurised-electro-slag re-melting (PERS) or by hot isostatic pressing (HIP) of nitrogen-containing powders. An
25 example of a nitrogen martensitic steel produced by PERS is SAE AMS 5898. The microstructure of SAE AMS 5898 typically comprises a fine martensitic matrix, made of units, and these units are decorated with carbo-nitrided particles and with a minor fraction of interlocked retained austenite regions. However, associated costs for producing martensitic steel by PERS or HIP are significantly high, for example higher
30 than pressure casting.

Another procedure for manufacturing high-nitrogen martensitic steels is adding of nitrogen to conventionally manufactured, low nitrogen, ferritic/martensitic steel components in the solid state by solution nitriding (SN). SN is a gaseous surface

treatment comprising the step of exposing a steel surface rich in alloying elements with high affinity to nitrogen, for example, chromium and manganese, to a nitriding atmosphere at a temperature where nitrogen is in solid solution in austenite, or where nitrogen is able to stabilize austenite. SN usually leads to a nitrogen enrichment up to a depth of 2.5 mm. As a result, thin-walled near-net-shape components can be through-nitrided such that the component is nitrided throughout the entire depth range, thereby reproducing the bulk chemical composition of PERS- and HIP-produced parts.

A challenge associated with SN is the coarsening of the microstructure as a consequence of, for example, long-time exposure of the material at a high temperature. The microstructure of SN samples is consequently significantly coarser than the one of cast and conventionally heat treated, comprising the steps of austenisation followed by quenching and tempering steps, particularly in the nitrogen-enriched case. Coarsening of the microstructure deteriorates the mechanical properties and hence the performance of these components in service.

Coarsening can be addressed based on the crystalline structure of the steel subjected to SN, i.e. austenitic, duplex, martensitic, ferritic. For example for martensitic steels, a double hardening process may be applied. The double hardening process comprises the step of applying a conventional hardening cycle at the end of the SN process as to exploit the phase transitions occurring during the thermal cycle to promote refinement. Nevertheless, the obtained microstructure is not equivalent to the one that is obtained in conventionally and HIP / PERS manufactured martensitic steels. Nitrogen-containing steel components can only be treated in a limited manner, because of the risk for nitride formation. Consequently, the martensitic microstructure cannot be modified to obtain a desired grain size by conventional methods as deformation and recrystallization.

Thus, there is a need for developing an approach for the manufacturing of a steel component comprising a fine-grained nitrogen-containing martensite structure component at low cost.

Thus, there is a need for developing an approach for the manufacturing of a steel component comprising a fine-grained nitrogen-containing martensite structure component with a controlled case depth range at low cost.

Summary

In general, the present disclosure concerns addition of nitrogen to stainless steel and microstructure/grain refinement of stainless steel at low cost. Additionally, the present disclosure concerns simultaneously working on the chemical composition and microstructure of the stainless steel for improving the performance of the stainless steel. With the present disclosure, a steel component can be processed such that a fine-grained hard microstructure of both the nitrogen-affected case and the bulk steel material can be obtained. The resulting fine-grained microstructure has several benefits over the coarse-grained structure, such as improved strength and ductility.

It is therefore an objective of the present disclosure to provide processes for improving the mechanical strength of stainless steel.

It is yet a further objective of the present disclosure to provide processes for the manufacture of a steel comprising a fine-grained martensitic structure over a certain depth range. Consequently, the depth range and the hardness of the nitrogen-affected case are controlled. Furthermore, thick components can be provided with a nitrogen-rich case, such that the nitrogen-enriched depth range is commensurate with the depth range where the heaviest loads need to be supported during application.

It is a further objective of the present disclosure to provide a high-nitrogen martensitic steel with improved strength, hardness, ductility, corrosion performance, wear characteristics and rolling contact fatigue resistance.

Yet another objective of the present disclosure is to provide products with fine grains in the nitrogen-enriched case as well as the bulk steel material.

The present disclosure therefore relates, in a first aspect, a process for the manufacture of a steel component comprising a fine-grained martensite structure component, the process comprising the steps:

- i) Providing a steel component having an initial steel composition;

- ii) Introducing nitrogen into the steel component at a temperature T1 above 950°C, thereby creating an at least partly austenitic nitrogen-containing steel component;
- 5 iii) Bringing the at least partly austenitic nitrogen-containing steel component to a temperature T2 below 950°C, preferably below 800°C, thereby decomposing austenite into a steel component comprising at least an amount of carbon- and/or nitrogen-containing precipitates;
- 10 iv) Bringing the steel component comprising at least an amount of carbon and/or nitrogen-containing precipitates to a temperature T3 which is above T2, thereby creating an at least partly austenitic nitrogen-containing steel component, optionally comprising at least an amount of carbon- and/or nitrogen-containing precipitates; and
- 15 v) Bringing the at least partly austenitic nitrogen-containing steel component to a temperature T4 that is below a martensite start temperature of the at least partly austenitic nitrogen-containing steel component for initiating transformation of at least some of the austenite
- 20 into fine-grained martensite, thereby producing a steel component comprising a fine-grained martensite structure component.

The present disclosure is based on the realization that soft annealing or normalising of a forged product promotes the formation of precipitates that are only partially dissolved

25 during subsequent hardening and that are fundamental to set the fine microstructure of the product. The present disclosure has therefore further realised that the introduction of an additional thermal step below 950°C, preferably below 800°C, decomposes austenite into a steel component comprising at least an amount of carbon and/or nitrogen-containing precipitates, thereby creating a condition for obtaining a fine and

30 high-nitrogen martensitic microstructure. This additional step can be referred to as a refinement step.

During the refinement step, the microstructure of the material evolves from a mixture of martensite and austenite into a tempered martensitic/ferritic or martensitic/austenitic or ferritic/austenitic matrix decorated with moderately fine and uniformly distributed

35 carbon- and nitrogen-containing particles. Specifically, based on a chosen temperature,

austenite can decompose into (carbo)nitrides and ferrite or (carbo)nitrides and nitrogen lean austenite. These carbon- and nitrogen-containing particles partially dissolve during subsequent hardening while ensuring the optimal conditions for keeping the structure very fine.

5

Generally, the present invention discloses a process which can allow for SN of conventional low-cost ferritic/martensitic steels, applied for replicating the properties of expensive PERS- and HIP-manufactured high-nitrogen martensitic steels in the surface region of large components, and/or over the entire cross section of near-net-shaped parts. A thermal step in between SN and a second hardening step can be introduced to replicate the microstructure of conventionally manufactured parts in SN components. As a result, the microstructure and composition of the - by the present disclosure - manufactured material are equivalent to the one obtainable with PERS / HIP.

However, a fundamental difference is that grain- and microstructure refinement in prior art SN is used only to synthesize an austenitic steel from a ferritic steel grade; hence, the material in prior art is ferritic to start with and austenitic in the end. In the present disclosure, the starting material may be either ferritic or martensitic (or a mixture thereof) to start with and it is martensitic at the end of the process. In prior art the nitrogen-rich precipitates are dissolved during a second high-temperature step in order not to impair the corrosion resistance and ductility of austenite. In the present disclosure, the process can be tailored so that these precipitates remain in the microstructure at the end of the process. Essentially, the overall evolution of the materials' microstructure as well as the results are significantly different in the hereby-proposed process. Advantageously, the present disclosure can provide products with a fine grain size in both the nitrogen-affected case and the bulk steel material, while the depth range of the nitrogen-affected case can be controlled.

In addition, nitriding in low alloyed steels and tool steels is generally performed in ammonia containing atmospheres at temperature not exceeding 590°C (so called ferritic nitriding). In association with carburizing processes, temperatures as high as 950°C are usually applied (so called austenitic nitrocarburizing). In both cases, deep nitrogen penetration is not obtained in an economically feasible manner. With the presently disclosed approach, an improved nitrogen introduction in depth can be obtained through nitriding at temperatures, such as exceeding of 950°C, preferably

above 1050 °C, more preferably above 1100°C. Then the steel component can be brought to T2, which can be below 950 °C. Then the component can be brought to T3, which is above T2. Thus, T3 can be above 950 °C.

- 5 Preferably, T2 can be below 800 °C. Accordingly, in a further embodiment T3 can be at least 850 °C. In general, the hardening effect can be enhanced based on the selected T3. In a further preferred embodiment, T3 is at least 900 °C.

10 The improvements achieved by the present disclosure can further be related to the Cr level of the initial steel, because a high content of Cr can allow for an improved N uptake. Furthermore, the higher the Cr the more N can be dissolved.

The present disclosure therefore further relates to, in a second aspect, a steel component comprising a fine-grained martensite structure component, wherein the
15 fine-grained martensite structure component is in the form of a case enveloping a core having a second structure component, wherein the core and the case are different, and further wherein the fine-grained martensite structure component is characterised by a composition comprising

- 20 a. 0.02 wt% to 3 wt% N;
b. 0.02 wt% to 3 wt% C; and
c. 4.5 wt% to 30 wt% Cr.

Consequently, the steel component as described herein can be used in various industrial fields.

25

One of the practical examples of the present disclosure may be the processing of bearing components, where the invention leads to surface properties and a microstructure similar to that of the expensive SAE AMS 5898 steel at the cost of a conventional low-nitrogen martensitic product. A further example of application of the
30 present disclosure may be modification of the process for tool steels where the coarse and soft microstructure obtained through conventional high temperature SN has hitherto limited the use of this process. The present disclosure allows a low-cost process route to obtain surface properties similar to expensive nitrogen-rich tool steels starting from conventional carbon-rich tool steel grades. The introduction of nitrogen
35 favours the dissolution of alloy carbides which is a prerequisite for subsequent

precipitation of carbo-nitrides from austenite; consequently a tailored distribution can be provided.

Description of the drawings

5 **Figure 1:** 1a is a schematic representation of one comparative thermal cycle applied in prior art double hardening as used in Example 1. 1b is a schematic representation of one exemplary thermal cycle applied according to the presently disclosed approach as used in Example 1.

10 **Figure 2:** 2a is a micrograph of the microstructure of X20Cr13 subjected to SN, hardening and refrigeration following the prior art double hardening process according to Fig. 1a as used in Example 1. 2b is a micrograph of the microstructure of X20Cr13 subjected to an exemplary thermal cycle following the cycle according to Fig. 1b.

15 **Figure 3:** shows an enlarged view of the microstructure of X20Cr13 subjected to the thermal cycle of Fig. 1b

Figure 4: shows the hardness profiles of X20Cr13 samples subjected to the process according to Fig. 1a and Fig. 1b as used in Example 1.

20

Figure 5: 5a is a schematic representation of one comparative thermal cycle applied in prior art double hardening as used in Example 2. 5b is a schematic representation of one exemplary thermal cycle applied according to the presently disclosed approach as used in Example 2.

25

Figure 6: 6a is a micrograph of the microstructure of X46Cr13 subjected to SN, hardening and refrigeration following the prior art double hardening process according to Fig. 5a as used in Example 2. 6b is a micrograph of the microstructure of X46Cr13 subjected to an exemplary thermal cycle, following the cycle in Fig. 5b as used in

30 Example 2.

Figure 7: shows an enlarged view of the microstructure of X46Cr13 subjected to the thermal cycle of Fig. 5b.

Figure 8: shows the hardness profiles of X46Cr13 subjected to the process according to Fig. 5a and Fig. 5b as used in Example 2.

5 **Figure 9:** 9a is a schematic representation of one exemplary thermal cycle as proposed by the presently disclosed approach having a refinement step of 2 hours as used in Example 3. 9b is a schematic representation of one exemplary thermal cycle proposed by the presently disclosed process having a refinement step of 6 hours as used in Example 3.

10 **Figure 10:** is a micrograph of the microstructure of X46Cr13 subjected to the thermal step in Fig. 9a. 10b a zoom of the microstructure of X46Cr13 subjected to the thermal step in Fig. 9b.

15 **Figure 11:** is a schematic representation of one exemplary thermal cycle proposed by the presently disclosed approach as used in Example 4.

Figure 12: is a micrograph of the microstructure of X20Cr13 subjected to the thermal cycle as disclosed in Fig. 11.

20 **Figure 13:** shows the hardness profile of X20Cr13 subjected to the thermal cycle as disclosed in Fig. 11.

Figure 14: is a schematic representation of one exemplary thermal cycle proposed by the presently disclosed approach as used in Example 5.

25

Figure 15: shows the hardness profile of X20Cr13 subjected to the thermal cycle as disclosed in Fig. 14.

30 **Figure 16:** is a micrograph of the microstructure of X38Cr14 subjected to the thermal cycle as disclosed in Fig. 14.

Figure 17: shows the hardness profile of X38Cr14 subjected to the thermal cycle in Fig. 14.

Figure 18: is a schematic representation of one exemplary thermal cycle proposed by the presently disclosed approach as used in Example 7.

5 **Figure 19:** is a micrograph of the microstructure of X38Cr14 subjected to the thermal cycle in Fig. 18.

Figure 20: shows the hardness profile of X38Cr14 subjected to the thermal cycle in Fig. 18.

10 **Figure 21:** is a micrograph of the microstructure of X46Cr13 subjected to the thermal cycle in Fig. 18.

Figure 22: shows the hardness profile of X46Cr13 subjected to the thermal cycle as disclosed in Fig. 18.

15

Detailed description

Specifically, the presently disclosed approach relates to a process for manufacturing of a steel component comprising a fine-grained martensite structure component. The steel component can be a component comprising a martensitic structure component.

20 The initial component may be a steel component having a composition characterised by comprising up to 2.0wt% C. The final manufactured component can be referred to as a steel component having a martensitic structure component. The martensitic structure component can comprise from 0.02 to 3 wt% C.

25 The fine-grained martensitic structure component can be a martensitic component having fine-grains. As referred herein, the fine-grain microstructure is a microstructure where the average size of the austenite grains that formed during step (iv) can be below 100 micrometres, preferably below 80 micrometres, more preferably below 50 micrometres.

30

The martensitic structure component can be characterised by a composition comprising 0.02 wt% to 3 wt% N.

In an embodiment, the fine-grained martensite structure component can be characterised by a composition comprising 0.02 wt% to 3 wt% N; 0.02 wt% to 3 wt% C; and 4.5 wt% to 30 wt% Cr.

5 Process step i)

An advantage of the presently disclosed approach is that the present disclosure allows an affordable process route to obtain surface properties similar to expensive nitrogen-rich tool steels, such as Vanax SuperClean® and Vancron 40 SuperClean®.

10 Conventional low-cost carbon-rich tool steel grades can thus by the present disclosure be treated by gas nitriding followed by heat treatment steps to obtain the improved mechanical properties associated with a fine-grained martensitic microstructure. Preferably, the hereby-disclosed process can be adapted to Cr-containing martensitic steel, such as martensitic stainless steels.

15 Thus, in one embodiment, the initial steel composition can comprise at least 4.5wt% Cr and at least 0.05wt% C. Alternatively, in one embodiment, the initial steel composition can comprise at least 10.5wt% Cr and at least 0.05wt% C. In a preferred embodiment, the initial steel composition can comprise 11.5 to 17.0wt% Cr and 0.1 to 1.0wt% C. In an embodiment, the initial steel composition can comprise 4.5 to 30wt% Cr and 0.05 to 2 wt% C. In an embodiment, the initial steel composition is characterised by comprising
20 0.01 to 0.1wt% N. Generally, Cr content remains unchanged during the process. The C content may increase, for example if carburizing prior to step ii) is applied. The steel component may therefore comprise up to 3wt% C.

25 An advantage of the presently disclosed process thereof is that the starting material can be martensitic and can remain martensitic at the end of the process, while having obtained a fine-grained martensitic microstructure.

Process step ii)

30 After providing a steel component having an initial steel composition in step i), the next step, step ii), is to introduce nitrogen at a temperature such that an at least partly austenitic nitrogen-containing steel component can be created. The steel component having an initial steel composition is therefore introduced to a high-temperature gas-nitriding step, wherein nitrogen is inserted into the material at a temperature T1 above 950°C, where austenite is stable, thereby creating an at least partly austenitic nitrogen-containing steel component.

Nitriding is a process used to diffuse nitrogen into the surface of a metal and is typically associated with enhanced mechanical properties. Media used for nitriding can, for example, be gas or plasma, as implemented in gas nitriding and plasma nitriding, respectively. In an embodiment, step ii) can comprise either gas nitriding or plasma nitriding. In an embodiment, step ii) can comprise only gas nitriding and/or plasma nitriding. The present approach, for example step ii) can be performed in an ammonia-free atmosphere. Furthermore, in a preferred embodiment, the introduction of nitrogen can be performed using a gas mixture comprising one or more of the following: ammonia, nitrogen, hydrogen, cyanides and/or argon. Nitriding may be provided by means of ammonia, nitrogen and/or other nitrogen-containing species that are gaseous at T1, while the carrier gas may comprise hydrogen, argon and/or other non-nitrogen-containing gases.

Additionally, the nitrogen-content can be selected based on desired mechanical properties. In an embodiment, the at least partly austenitic nitrogen-containing steel component can comprise nitrogen in the range 0.03-3.0wt% following the process in step ii). Based on desired mechanical properties, the nitrogen content can be varied. Thus in one embodiment, the nitrogen content may be in the range 0.03-0.1wt%, such as 0.1-0.5wt%, such as 0.5-1.0wt%, such as 1.0-1.5wt%, such as 1.5-2.0wt%, such as 2.0-2.5wt%, such as 2.5-3.0wt%.

As described above, nitrogen is inserted into the material at temperature T1 above 950°C, where austenite is stable. In an embodiment, temperature T1 can be above 1000°C, such as equal to or above 1100°C, such as equal to or above 1150°C, such as equal to or above 1200°C, with the prerequisite that the T1 is still below the melting point of the steel component.

In an embodiment, a carburizing step or a carbo-nitriding step can be applied prior to the step ii).

Process step iii)

Nitriding in step ii) can be followed by decomposition of austenite in step iii). The at least partly austenitic nitrogen-containing steel component therefore can be brought to an isothermal heat-treatment-step at a temperature where austenite is not stable and can decompose, and where precipitates can form. Thus, the at least partly austenitic

nitrogen-containing steel component is brought to a temperature T2 below 950°C, thereby decomposing austenite in a steel component comprising at least an amount of carbon- and/or nitrogen-containing precipitates. In an embodiment, the temperature T2 can be below 850°C, such as equal to or below 800°C, such as equal to or below 750°C, such as equal to or below 650°C. In an embodiment, the temperature T2 is between 500 and 800°C, preferably between 600 and 750°C, more preferably between 700 and 750°C. The temperature of the decomposition of the austenite may depend on the material composition of the steel component. In most, if not all material composition of the present approach, the temperature of the decomposition of the austenite can be below 800 °C.

This step iii) can be regarded as an isothermal heat treatment step or refinement step, which may be necessary to refine the microstructure of steels containing a large fraction of carbon and nitrogen. Introduction of the isothermal step may take place between hardening processes such as between nitriding and austenisation or between nitriding and quenching or between quenching and austenitisation. Thus, the isothermal heat treatment step can be performed immediately after high-temperature gas nitriding at a temperature below the gas nitriding temperature and/or where austenite is not stable or directly prior to heating to the austenitization temperature. Alternatively, the isothermal heat-treatment-step can be a self-standing thermal step.

Advantageously, the isothermal heat treatment step can yield a fine-grained, nitrogen-rich, hard microstructure in conventional mass-produced low-cost martensitic stainless steels, because nitrogen rich precipitates observed in step iii) are important for obtaining a desired fine-grained microstructure of the product. In one embodiment, the nitrogen-containing precipitates may be in the form of nitrides. In one embodiment the carbon-containing precipitates may be in the form of carbides. In one embodiment, the steel component, such as the core of the steel component, produced in step iii) can further comprise retained austenite in an amount equal to or less than 50%, such as less than 40%, such as less than 30%, such as less than 20%, such as less than 10%.

In one embodiment, the steel component produced in step iii) can further comprise retained austenite in a range from 50% to 0%, such as from 50% to 40%, such as from 40% to 30%, such as from 30% to 20%, such as from 20% to 15%, such as from 15% to 10%, such as from 10% to 5%, such as from 5% to 0%.

Process step iv)

After the refinement step iii), in step iv) austenite is stable and formed, and the grain growth is limited by the precipitates formed in the previous step iii). The steel component comprising at least an amount of carbon- and/or nitrogen-containing precipitates is therefore brought to a temperature T3 which is above T2, thereby creating an at least partly austenitic nitrogen-containing steel component. In an embodiment, the temperature T3 is at least 900 °C, preferably between 900 °C and 1150 °, preferably between 980 °C and 1150 °C, preferably between 1000 °C and 1100°C. Furthermore, in one embodiment, the temperature T3 in step iv) can be at a temperature below T1, such as at a temperature that does not exceed the melting point of the steel component.

Said steel component can comprise at least an amount of carbon- and/or nitrogen-containing precipitates. Consequently, the austenisation of step iv) and/or carbon- and/or nitrogen-containing precipitates can play a significant role in the formation of the fine-grained martensite structure component. In an embodiment, the fine-grained martensite structure component is formed from austenite grains of step iv) having a grain size of less than 50 µm. In one embodiment, the austenite grains of step iv) have a grain size of less than 40 µm, such as less than 30 µm, such as less than 25 µm, such as less than 20 µm, such as less than 15 µm, such as less than 10 µm, such as less than 5 µm.

In one embodiment, the austenite grains of step iv) have a grain size in a range from 50 µm to 0 µm, such as from 50 µm to 40 µm, such as from 40 µm to 30 µm, such as from 30 µm to 20 µm, such as from 20 µm to 15 µm, such as from 15 µm to 10 µm, such as from 10 µm to 5 µm, such as from 5 µm to 1 µm.

In one embodiment, the at least partly austenitic nitrogen-containing steel component produced in step iv) comprises retained austenite in an amount equal to or less than 40%, such as less than 35%, such as less than 30%, such as less than 25%, such as less than 20%, such as less than 15%, such as less than 10%, such as less than 5%.

Additionally, prior to step iii) and/or iv) the steel component can be taken to a temperature which is below 600°C, such as below 400°C, such as below 200°C, such as below 100°C, to produce phases and/or microstructures comprising carbides and

nitrides. The phases and/or microstructure can preferably comprise carbides, nitrides and a metallic matrix of ferrite, martensite and austenite. In an embodiment, the temperature can be between -200 °C and 750°C.

5 A great advantage of the present approach may be to introduce a fine, nitrogen containing martensitic structure. Because the present approach can comprise a refinement step (decomposition) after a nitriding step and before a hardening step. The order of the steps can provide exploiting the product of the austenite decomposition as a starting point, which further enhances obtaining a hard and fine structure.

10 In an embodiment, step iii) and/or step iv) are performed within an inert atmosphere comprising one or more of the followings: nitrogen, argon and/or helium. In an embodiment, step iii) is performed under vacuum. In an embodiment step iii) and/or step iv) are performed under the pressure of at least 0.15 bar, preferably between 0.15 and 15 bars, more preferably between 0.25 and 15 bars.

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Process step v)

The next step of the presently disclosed process is quenching the steel component to form fine-grained martensite. Quenching can be to room temperature or to a temperature lower than 0°C. Thus, the at least partly austenitic nitrogen-containing
20 steel component is brought to a temperature T₄ that is below a martensite start temperature of the at least partly austenitic nitrogen-containing steel component such that transformation of at least some of the austenite into fine-grained martensite can be initiated. At least some of the austenite may be at least 50% of the austenite, preferably at least 80% of the austenite. Accordingly, parts of the steel component can comprise a
25 dominating fraction of martensitic microstructure. As a result, a steel component comprising a fine-grained martensite structure component can be produced.

In an embodiment, step iv) and step v) are performed at a pressure between 0.15 and 15 bar, preferably between 0.25 and 15 bar, more preferably between 0.25 and 10 bar, more preferably between 0.36 and 4 bar.

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Process step vi)

Furthermore, in an embodiment, the process can comprise an additional step, step vi) comprising tempering the steel component at least once in the temperature range of 60°C to 700°C. An advantage of one or more tempering cycles is that through

tempering, the materials properties, such as toughness, can be adapted to a specified application. The tempering temperature and tempering cycles can be specified based on the desired mechanical properties. In a further embodiment, the process can comprise a thermal treatment at least once at sub-zero Celsius temperature between
5 step v) and step vi), such as at temperatures ranging from -200°C to 0°C, such as -150°C to 0°C, such as -100°C to 0°C.

The present disclosure relates to a process for manufacturing of a steel component comprising a fine-grained martensite structure component characterised by a
10 composition. In one embodiment, the fine-grained martensite structure component can be in the form of a case enveloping a core having a second structure component, wherein the second structure component is different from the fine-grained martensite structure component. In a preferred embodiment, the fine-grained martensite structure component can be in the form of a case, wherein the case may have a depth range in
15 the range 0.05-30 mm, such as 0.05-20 mm, such as 0.05-10 mm.

Furthermore, the present disclosure relates to a steel component comprising a fine-grained martensite structure component obtained according to any one of the processes hereby-disclosed. In an embodiment, the fine-grained martensite structure
20 component can be characterised by a composition comprising 0.02 wt% to 3 wt% N; 0.02 wt% to 3 wt% C; and 4.5 wt% to 30 wt% Cr. In one embodiment, the fine-grained martensite structure component can be in the form of a case surrounding a core having a second structure component which is different from the fine-grained martensite structure component. Thus, when a bulk material is processed with the hereby-
25 proposed procedure, a fine-grained martensitic case around the bulk material may be obtained.

In one embodiment, the fine-grained martensite structure component can be in the form of a case surrounding a core having a second structure component, wherein the
30 core structure component is identical to the fine-grained martensite structure component of the case.

The fine-grained martensite structure may for example have the following composition 13%Cr, 0.4%C, 0.3%N, 0.5%Si, 0.5%Mn, Ni, Cu and impurities such as S, P, O, in the
35 ppm range, balance Fe.

The fine-grained martensite structure may for example have the following composition 17%Cr, 1%Mo, 0.8%C, 0.6%N, 0.5%Si, 0.5%Mn, Ni, Cu, and impurities such as S, P, O, in the ppm range, balance Fe.

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The fine-grained martensite structure may for example have the following composition 5%Cr, 1%C, 0.2%N, 0.5%Si, 0.5%Mn, Ni, Cu and impurities such as S, P, O, in the ppm range, balance Fe.

10 The fine-grained martensite structure may for example have the following composition 12%Cr, 1.5%C, 0.3%N, 0.5%Si, 0.5%Mn, Ni, Cu, and impurities such as S, P, O, in the ppm range, balance Fe.

15 The fine-grained martensite structure may for example have the following composition 15%Cr, 1%Mo, 0.3%C, 0.4%N, 0.5%Si, 0.5%Mn, Ni, Cu, and impurities such as S, P, O, in the ppm range, balance Fe.

Steel component

20 The present disclosure relates to a steel component comprising a fine-grained martensite structure component. Preferably, the fine-grained martensite structure component of the steel component can be in the form of a case surrounding a core. The core may have a second structure component such that the core and the case are different. Differences can entail for example that the core can contain less nitrogen than the case, and/or the core can contain different types of precipitates than the case, and/or the core can contain a different fraction of austenite and/or of carbon and/or of nitrogen containing precipitates than the case, and/or the core can be softer than the case, and/or the core can have coarser microstructural features than the case.

30 Preferably, the fine-grained martensite structure component can be characterised by a composition comprising 0.02 wt% to 3 wt% N; 0.02 wt% to 3 wt% C; and 4.5 wt% to 30 wt% Cr.

35 In an embodiment, the nitrogen level in the core of the steel component is lower than the nitrogen level in the case of the steel component. An advantage of higher nitrogen level in the case may be increased hardness and strength without increasing the

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brittleness due to preserved toughness in the core. This foresees that the hardness can increase from the core to the case of the steel component. In an embodiment, the fine-grained martensite structure component has a hardness in the range of 300-1400 HV1. In one embodiment, the hardness of the fine-grained martensite structure component is in the range of 300-500 HV1, such as 500-600 HV1, such as 600-700 HV1, such as 700-800 HV1, such as 800-900 HV1, such as 900-1000 HV1, such as 1000-1200 HV1, such as 1200-1400 HV1. Furthermore, the case with higher nitrogen level can have various depth ranges. In an embodiment, the case has a depth range in the range from 0.05-30 mm, such as 0.05-1.0 mm, such as 1.0 to 2.0 mm, such as 2.0 to 5.0 mm, such as 5.0 to 10 mm, such as 10 to 20 mm, such as 20 to 30 mm.

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The mechanical properties of the fine-grained martensite structure component, such as the depth and the hardness of the case can highly depend on the austenisation and/or carbon- and/or nitrogen-containing precipitates. In one embodiment, the fine-grained martensite structure component is formed from austenite grains, wherein the austenite grains, prior to transformation into the fine-grained martensite structure component, have a grain size of less than 50 μm . In one embodiment, the austenite grains, prior to transformation into the fine-grained martensite structure component, have a grain size of less than 40 μm , such as less than 30 μm , such as less than 25 μm , such as less than 20 μm , such as less than 15 μm , such as less than 10 μm , such as less than 5 μm . In one embodiment, the austenite grains, prior to transformation into the fine-grained martensite structure component have a grain size in a range from 50 μm to 1 μm , such as from 50 μm to 40 μm , such as from 40 μm to 30 μm , such as from 30 μm to 20 μm , such as from 20 μm to 15 μm , such as from 15 μm to 10 μm , such as from 10 μm to 5 μm , such as from 5 μm to 1 μm .

In a preferred embodiment, the fine-grained martensite structure component and/or the second structure component may not be identical to SAE AMS 5898.

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In a preferred embodiment, the fine-grained martensite structure component and the second structure component may not both be identical to SAE AMS 5898.

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Additionally, the steel component may further comprise alloying elements, i.e., elements of the periodic table. In an embodiment, the steel component may further comprise at least one other alloying element. In a further embodiment, the at least one

alloying element can be one or more selected from Si, Mo, Mn, Nb, V, Ta, Ti, Ni, Cu and Co.

Application area

5 The hereby-disclosed steel component can be used in a wide range of industrial applications. In one embodiment, the steel component as defined herein can, for example, find usage in bearings, gears, crankshafts, screws, tools, weapons, armours, knives, medical and/or dental utensils.

10 In an embodiment, the steel component as defined herein can be used for preventing white etching cracks in bearings. Mechanical and thermal stresses acting on the steel components can cause a variety of failure modes, such as white etching cracks. Especially in the bearing industry, one of the root causes of failure is white etching cracks, which may be related to rolling-contact fatigue.

15 An advantage of the present disclosure is providing a high-performance steel component such that some of the failure modes can be prevented. For example, in an embodiment, the steel component as defined herein for (use in/prevention of) rolling and/or sliding contact fatigue.

20 In an embodiment, the steel component as defined herein can be used in wind turbine components. White etching cracks are especially common in the wind turbine industry and can shorten the expected lifetime of a wind turbine significantly. White etching cracks can be considered as one of the most expensive technical failure modes for a
25 wind turbine. Thus, the hereby proposed processes, products and usage may be of interest for the bearing industry because of immunity to the formation of white etching cracks.

Examples

Example 1

30 In a first example, the presently disclosed process was applied to steel grade X20Cr13 and the effect of the treatment was compared to the one obtained by double hardening as disclosed in [1, 2].

35 Samples were two cubes of 20x20x20 mm³, which were cut out of a hot rolled bar in soft annealed condition and supplied by Böhler Edelstahl GmbH & Co.

Fig. 1a is a schematic representation of one embodiment of thermal cycles applied in double hardening while Fig. 1b shows a schematic representation of one embodiment of thermal cycles applied according to any of the processes of the presently disclosed invention.

Samples were SN in nitrogen gas at $1150 \pm 20^\circ\text{C}$ for 4 hours. The treatment was performed in a custom-made hot wall furnace subjected to complete renewal of the nitrogen atmosphere once a minute. The pressure was controlled with an accuracy of approximately 10 mbar and kept at 3 bar for the first 3 hours of treatment, followed by SN at 2 bar during the last hour. Following SN, samples were gas-quenched in nitrogen to room temperature at a gas pressure of 4 bars.

Following SN, the sample of proposed treatment was treated in nitrogen at 700°C for 2 hours and furnace cooled as shown in Fig. 1b, while the sample of double hardening was maintained at room temperature. Both samples were then subjected to a (second) hardening cycle consisting in austenitisation at 1050°C at 0.7 bar nitrogen pressure for 0.5 hours followed by gas quenching. The quenching parameters were identical to the ones described above and following SN. Finally, the samples were refrigerated for 4 hours by storage in "dry ice", sublimating CO_2 (i.e., at -78°C).

The two samples were investigated in the cross section. Metallographic investigation was performed after hot moulding at 180°C for 5 minutes followed by mirror polishing. Hardness measurements were performed using a Future Tech model FM-700 micro-hardness tester equipped with a Vickers indenter applying a load of 0.5 kg and a dwell time of 10 s. Optical microscopy was performed with an Olympus GX 41 microscope equipped with a Leica DFC 450 C camera. To reveal the microstructure of the material, samples were immersed in Viella reagent for 20 s (sample 1A, proposed process) and 16 s (sample 1B, double hardening).

Fig. 2a and 2b show embodiments of the result of the thermal treatments as revealed by optical microscopy applied at low magnification. Fig. 2a is one embodiment of the microstructure of X20Cr13 subjected to SN, hardening and refrigeration, i.e., the double hardening process according to Fig. 1a and shows that relatively coarse martensitic structure as obtained by the double hardening process is visible over the

material cross section. The surface of the materials 2, 2' are the top surface in Fig. 2a and 2b while the bulk region 3, 3' are at the bottom of the figures. In comparison, the process run according to the proposed invention yields a significantly finer microstructure as shown in Fig. 2b, in particular in the first 300 micrometres below the sample surface 2'. The presence of fine precipitates is also clearly visible in the near-surface region, where these appear concentrated in bands 4 perpendicular to the surface 2'. These bands 4 are reminiscent of macro-segregation in the as-received material, which are more easily revealed in the case of the material treated according to the proposed process but are actually present in both samples. In the sample subjected to double hardening, precipitation appears in terms of a continuous network at the prior austenite grain boundary and macro-segregation is less visible.

One embodiment of the enlargement of the microstructure in Fig. 2b is presented in Fig. 3 and allows appreciating the fine scale of the obtained nitrogen-rich martensitic microstructure in the near surface region of the sample, where this is revealed by the presence of etchant reacting precipitates at boundaries.

Furthermore, Fig. 4. shows embodiments of hardness profiles of X20Cr13 subjected to the processes according to Fig. 1a and Fig. 1b. Fig. 4 shows clearly that especially at the sample surface, the proposed process appears to yield a better hardening effect. Overall, the surface hardness reaches up to 720 HV, while the bulk hardness is in the order of 580 HV. These values are appropriate for bearings, knives and other demanding applications where martensitic stainless steels find widespread usage.

Example 2

In another example, the proposed process was applied to steel grade X46Cr13 and the effect of the presently disclosed treatment was compared to the one obtained by double hardening [1, 2].

Samples were two cubes, approximately 20x20x20 mm³, which were cut from a hot rolled bar provided in soft annealed condition. The samples were supplied by DEW-Stahl GmbH & Co. Samples were subject to thermal cycles as disclosed in Fig. 5a and Fig. 5b. Fig. 5a is a schematic representation of one embodiment of thermal cycles applied in double hardening while Fig. 5b shows a schematic representation of one

embodiment of thermal cycles applied according to any of the processes of the presently disclosed invention.

SN was applied as first treatment step with parameters identical to the ones presented above for example 1. Similarly, one of the cubes was treated at 700°C for 2 hours while the other was maintained at room temperature. Hardening was performed at 1000°C at 0.36 bar for 0.5 hours and was again followed by gas quenching in nitrogen at an applied pressure of 4 bar. Refrigeration was applied after hardening and consisted of storage for 4 hours in sublimating dry ice, i.e. solid CO₂, at approx. -78 °C.

Sample preparation, experimental methods and analysis methods were similar to the ones presented for example 1, albeit for a fixed etching time of 18 s.

Figs. 6 and 7 show the beneficial effect of the proposed process on the microstructure of SN X46Cr13. The micrograph in Fig. 6a refers to the material subjected to double hardening and shows a coarse martensitic microstructure with a large fraction of retained austenite concentrated along (macro-segregation) bands perpendicular to the sample surface. Martensite units of several dozen micrometres in length are clearly visible. Evidently, double hardening does not cope with the coarsening of the microstructure as introduced by SN. Conversely Fig. 6b, the microstructure of the material treated by introducing an intermediary step in between SN and the second hardening cycle results in a very fine martensitic microstructure, especially in the near surface region, as can be appreciated in Fig. 7. In particular, in the near surface region, the microstructure is so fine that it cannot be resolved by optical microscopy, indicating nanometre-sized features. Furthermore, Fig. 6b shows macro segregation bands perpendicular to the sample surface and retained austenite observed in regions partitioned by dark martensite plates.

Regarding hardness, the hardening profile in Fig. 8 indicates that the bulk hardness of the two samples is in the order of 660 HV and 640 HV for the sample treated according to the proposed process as shown in Fig. 5b versus the sample subjected to a trivial double hardening process as shown in Fig. 5a, respectively. The surface hardness approaches 780 HV for the sample treated according to an embodiment of the presently disclosed process, while double hardening yields a surface hardness of approximately 760 HV. The hardness difference both in the bulk and in the near

surface region reflects a different content of retained austenite in the samples summed up with refinement of the microstructure by the proposed process.

Thus, these results show that the presently disclosed process enhanced the hardness profile of a sample not only in the core of the sample but also on the case (outer layer) of the sample.

Example 3

In example 3, the material under investigation was X46Cr13 supplied by DEW-Stahl GmbH & Co. Starting material conditions and samples' geometry were similar to those described above for example 2. The samples were firstly subjected to SN applying the above-described parameters. Thereafter, a hardening cycle was applied wherein heating to the austenitisation temperature was interrupted for an isothermal step at 700°C of 2 hours and 6 hours, for samples 3A and 3B, respectively. After annealing at 700°C, the material was directly austenitised (no cooling in between) at 1050°C at 0.36 bar for 0.5 hours. When compared to examples 1 and 2, the intermediate thermal step in between SN and hardening was introduced directly in the hardening cycle, and specifically during heating to the hardening temperature, rather than as a self-standing step. Gas quenching and refrigeration followed and were accomplished as described above (example 1). The thermal cycle are represented in Fig. 9a and 9b. Sample preparation and metallographic investigation was as described in example 1 with an etching time as described in example 2.

Fig. 10a and 10b show the microstructure of the material for the two thermal cycles as shown in Fig. 9a and 9b, respectively. In both cases, the microstructure is of a martensitic steel with fine precipitates that cannot be resolved by optical microscopy. Extremely fine features are visible in the near-surface region (22, 22'), while the microstructure of the material in the region ranging from a few hundred micrometres below the surface to the bulk region (i.e. > 1 mm) present coarser features. Macro segregation bands (24, 24') perpendicular to the sample surface are indicated with dashed rectangles and retained austenite (26, 26') observed in regions partitioned by dark martensite plates are shown in Fig 10a and 10b. Overall, the scale of the microstructure was the smaller the longer the thermal step at 700°C. Upon isothermal holding at 700°C for 6 hours, the structure appears largely fine and homogeneous along the full cross section.

In examples 1-3, an additional thermal step was introduced in between SN and hardening to promote refinement of the microstructure of the nitrogen-rich martensitic steel case obtained on carbon martensitic samples. The thermal step was applied either as a self-standing thermal step or in connection with the hardening cycle. Similar effect is obtained by interrupting the cooling step from the SN temperature to room temperature in favour of an isothermal step. Moreover, a very fine martensitic microstructure is obtained in near-net-shape components where SN time is sufficiently long to through-nitride the steel part and the treatment is followed by the thermal step hereby proposed prior to a second hardening cycle.

Example 4

In the fourth example, the process was similar to the one applied in example 1 as shown in Fig. 1b, but for a final step of tempering for 2 hours at the end of the thermal cycle. Moreover, the sample was an FE8 test ring that was heat-treated in an industrial furnace optimized for SN. Quenching was performed using 10 bar pressured nitrogen gas. Sample preparation and investigational methods are according to the ones reported for examples 1-3. The thermal cycle is presented in Fig. 11.

An embodiment of the microstructure given in Fig. 12 shows only minor differences when compared to the example 1 shown in Fig. 3. Additionally, an embodiment of the hardness profile provided in Fig. 13 indicates that final tempering at 250°C reduced the hardness of the material by approximately 20 HV. Tempering can be applied to release internal stresses in the martensite structure and improve toughness. Applications for this material may be the ones listed for example 1 and elsewhere in the present application.

Example 5

In the fifth example, X20Cr13 supplied by Böhler Edelstahl GmbH & Co was subjected to the same thermal cycle applied for example 4, but for the final tempering cycle that was at 470°C instead of 250°C, as shown in Fig. 14. Hardness profile in Fig. 15 shows that tempering at 470°C brought surface hardness to 730 HV. Tempering in the secondary hardening region, such as between 450°C-520°C, is advantageous for applications that require maximum hardness and strength.

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Example 6

In the sixth example, thermal cycle and set up were as described for example 5. The material under investigation was grade X38Cr14 Stavax® supplied by Uddeholm A/S in form of soft annealed rod. This steel grade is applied for tooling applications.

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Fig. 16 shows an embodiment of a uniform and fine martensitic microstructure. As shown in Fig. 17, the corresponding hardness is in the range of 680-750 HV. The absence of (macro-segregation) bands is a consequence of the production route for the Stavax® material supplied by Uddeholm A/S, which is manufactured by electro-slag remelting (ESR). The effect of nitrogen on the hardness of the material is reflected by the hardness profile. This material solution is highly relevant for the application of high-end martensitic stainless steels.

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Example 7

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In the seventh example, the thermal cycle as proposed in the hereby-disclosed invention was repeated multiple times. Fig. 18 shows the thermal cycle implemented in example 7. Herein, after SN, isothermal holding followed by hardening was repeated twice and finalised with cryogenic treatment and two tempering cycles. Both X46Cr13 and X38Cr14 were investigated by applying the specified thermal cycle. The industrial set up was applied in all experiments and sample geometry was based on FE8 test ring type. Details of the thermal cycle is described below.

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For the thermal cycle of example 7 shown in Fig. 18, the following procedure was applied: SN at $1150 \pm 20^\circ\text{C}$ for 7 hours, of which 5 hours applying 3 bar nitrogen and 2 hours applying 0.65 bar; isothermal annealing at 680°C for 6 hours; hardening by austenitisation at 1080°C for 0.5 hours at 0.45 bar pressure followed by gas quenching; isothermal holding at 680°C for 6 hours; hardening by austenitisation at 1010°C for 0.5 hours at 0.15 bar pressure followed by gas quenching; refrigeration at -80°C for 8 hours in dry ice; and double tempering 2x2 hours at 250°C .

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Data referring to example 7 is reported in Figs. 19-22. An embodiment of the microstructure and the relative hardness profile for X38Cr14 steel grade are shown in Fig. 19 and 20, respectively. Fig. 21 and 22 are embodiments of the microstructure and relative hardness profile for X46Cr13 steel grade, respectively.

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Comparing Figs. 19 and 21 with the microstructures of all the previous examples clearly reveals that applying the proposed process twice promotes additional homogenisation and refinement of the microstructure, in spite of an initial SN treatment of almost double duration (7 hours instead of 4 hours). The proposed processing has
5 resulted in a case depth of 1.5 to 2 mm, having a nitrogen-rich fine martensitic structure for both steels.

Reference list:

- [1] M.H. Evans, "An updated review: white etching cracks (WECs) and axial cracks in
10 wind turbine gearbox bearings", Mater. Sci. Technol. 32:11 (2016) 1133-1169.
[2] H. Berns, S. Siebert, "Randaufsticken nichtrostender Stähle", HTM Haertere Tech.
Mitt. 49 (1994) 123-128.

Items

- 15 1. A process for the manufacture of a steel component comprising a fine-grained
martensite structure component, the process comprising the steps:
- i) Providing a steel component having an initial steel composition;
- 20 ii) Introducing nitrogen into the steel component at a temperature T1
above 950°C, thereby creating an at least partly austenitic nitrogen-
containing steel component;
- 25 iii) Bringing the at least partly austenitic nitrogen-containing steel
component to a temperature T2 below 950°C thereby decomposing
austenite into a steel component comprising at least an amount of
carbon- and/or nitrogen-containing precipitates;
- 30 iv) Bringing the steel component comprising at least an amount of
carbon- and/or nitrogen-containing precipitates to a temperature T3
which is above T2, thereby creating an at least partly austenitic
nitrogen-containing steel component optionally comprising at least
an amount of carbon- and/or nitrogen-containing precipitates; and

- 5 v) Bringing the at least partly austenitic nitrogen-containing steel component to a temperature T₄ that is below a martensite start temperature of the at least partly austenitic nitrogen-containing steel component for initiating transformation of at least some of the austenite into fine-grained martensite, thereby producing a steel component comprising a fine-grained martensite structure component.
- 10 2. The process according to any one of the preceding items, wherein the initial steel composition is characterised by comprising at least 4.5wt% Cr and 0.05wt% C.
- 15 3. The process according to any one of the preceding items, wherein the initial steel composition is characterised by comprising at least 10.5wt% Cr and 0.05wt% C.
4. The process according to any one of the preceding items, wherein the initial steel composition is characterised by comprising 11.5 to 17.0wt% Cr and 0.1 to 1.0wt% C.
- 20 5. The process according to any one of the preceding items, wherein the at least partly austenitic nitrogen-containing steel component comprises nitrogen in the range of 0.03-3.0wt% following the process in step ii).
6. The process according to any one of the preceding items, wherein the steel component produced in step iii) further comprises retained austenite in an amount equal to or less than 50%.
- 25 7. The process according to any one of the preceding items, wherein the fine-grained martensite structure component is characterised by a composition comprising:
- 30 a. 0.02 wt% to 3 wt% N;
- b. 0.02 wt% to 3 wt% C; and
- c. 4.5 wt% to 30 wt% Cr.

8. The process according to any one of the preceding items, wherein the fine-grained martensite structure component is formed from austenite grains of step iv) having a grain size of less than 50 μm .
- 5 9. The process according to any one of the preceding items, comprising an additional step, step vi) comprising tempering the steel component at least once in the temperature range of 60°C to 700°C.
- 10 10. The process according to any one of the preceding items, comprising a thermal treatment at least once at sub-zero Celsius temperature between step v) and step vi), such as at temperatures between -200°C to 0°C, such as -150°C to 0°C, such as -100°C to 0°C.
11. The process according to any one of the preceding items, wherein step ii) comprises either gas nitriding or plasma nitriding.
- 15 12. The process according to any one of the preceding items, wherein introducing nitrogen is performed using a gas mixture comprising one or more of ammonia, nitrogen, hydrogen, cyanides and/or argon.
- 20 13. The process according to any one of the preceding items, wherein prior to step iii) and/or iv) the steel component is/are taken to a temperature which is below 600°C, such as below 400°C, such as below 200°C, such as below 100°C, to produce phases comprising or consisting of carbides, nitrides, and/or metal alloys.
- 25 14. The process according to any one of the previous items, wherein the temperature T1 is above 1000°C, such as equal to or above 1100°C, such as equal to or above 1150°C, such as equal to or above 1200°C, with the prerequisite that the T1 is still below the melting point of the steel component.
- 30 15. The process according to any one of the previous items, wherein the temperature T2 is below 850°C, such as equal to or below 800°C, such as equal to or below 750°C.
16. The process according to any one of the previous items, wherein the temperature T3 in step iv) is at a temperature below T1, such as at a temperature that does not exceed the melting point of the steel component.

17. The process according to any one of the previous items, wherein the fine-grained martensite structure component is in the form of a case surrounding a core having a second structure component, which is different from the fine-grained martensite structure component.
- 5 18. The process according to any one of the previous items, wherein the fine-grained martensite structure component is in the form of a case, wherein the case has a depth range in the range from 0.05-30 mm, such as 0.05-20 mm, such as 0.05 to 10 mm.
- 10 19. A steel component comprising a fine-grained martensite structure component obtained by the process according to any one of the preceding items, wherein the fine-grained martensite structure component is characterised by a composition comprising:
- 15 a. 0.02 wt% to 3 wt% N;
 b. 0.02 wt% to 3 wt% C; and
 c. 4.5 wt% to 30 wt% Cr,
 wherein the fine-grained martensite structure component is in the form of a case surrounding a core having a second structure component which is different from the fine-grained martensite structure component.
- 20 20. A steel component comprising a fine-grained martensite structure component, wherein the fine-grained martensite structure component is in the form of a case surrounding a core having a second structure component, wherein the core and the case are different, and further wherein the fine-grained martensite structure component is characterised by a composition comprising
- 25 a. 0.02 wt% to 3 wt% N;
 b. 0.02 wt% to 3 wt% C; and
 c. 4.5 wt% to 30 wt% Cr.
21. The steel component according to item 20, wherein the steel component comprises at least an amount of carbon- and/or nitrogen-containing precipitates.
- 30 22. The steel component according to item 21, wherein the nitrogen level in the core is lower than the nitrogen level in the case.

23. The steel component according items 20-22, wherein the fine-grained martensite structure component has a hardness in the range of 300-1400 HV1.
24. The steel component according to items 20-23, wherein the fine-grained martensite structure component is formed from austenite grains, wherein the austenite grains, prior to transformation into the fine-grained martensite structure component, have a grain size of less than 50 μm .
25. The steel component according to items 20-24, wherein the case has a depth in the range of 0.05-30 mm, such as 0.05-20 mm, such as 0.05 to 10 mm.
26. The steel component according items 20-25, wherein the fine-grained martensite structure component and/or the second structure component is/are not identical to SAE AMS 5898.
27. The steel component according to items 20-26, further comprising at least one other alloying elements.
28. The steel component according to items 20-27, wherein the at least one alloying elements are one or more selected from Si, Mo, Mn, Nb, V, Ta, Ti, Ni, Cu and Co.
29. A steel component according to any one of items 19-28 for use in bearings, gears, crankshafts, screws, tools, weapons, armours, knives, medical and/or dental utensils.
30. A steel component according to any one of items 19-28 for use in wind turbine components.
31. A steel component according to any one of items 19-28 for use preventing white etching cracks in bearings.
32. A steel component according to any one of items 19-28 for use in and/or for prevention of rolling and/or sliding contact fatigue.

Claims

1. A process for the manufacture of a steel component comprising a fine-grained martensite structure component, the process comprising the steps:

5

vi) Providing a steel component having an initial steel composition;

10

vii) Introducing nitrogen into the steel component at a temperature T1 above 950°C, thereby creating an at least partly austenitic nitrogen-containing steel component;

15

viii) Bringing the at least partly austenitic nitrogen-containing steel component to a temperature T2, wherein T2 is below 800°C, such that austenite is decomposed into a steel component comprising at least an amount of carbon- and/or nitrogen-containing precipitates;

20

ix) Bringing the steel component comprising at least an amount of carbon- and/or nitrogen-containing precipitates to a temperature T3 which is above T2, wherein T3 is preferably above 900°C, thereby creating an at least partly austenitic nitrogen-containing steel component optionally comprising at least an amount of carbon- and/or nitrogen-containing precipitates; and

25

x) Bringing the at least partly austenitic nitrogen-containing steel component to a temperature T4 that is below a martensite start temperature of the at least partly austenitic nitrogen-containing steel component for initiating transformation of at least some of the austenite into fine-grained martensite, thereby producing a steel component comprising a fine-grained martensite structure component.

30

2. The process according to any one of the preceding claims, wherein the initial steel composition is characterised by comprising at least 4.5wt% Cr and 0.05wt% C.

35

3. The process according to any one of the preceding claims, wherein the initial steel composition is characterised by comprising at least 10.5wt% Cr and 0.05wt% C.
- 5 4. The process according to any one of the preceding claims, wherein the initial steel composition is characterised by comprising 11.5 to 17.0wt% Cr and 0.1 to 1.0wt% C.
- 5 5. The process according to any one of the preceding claims, wherein the initial steel composition is characterised by comprising 0.01 to 0.1wt% N.
- 10 6. The process according to any one of the preceding claims, wherein the at least partly austenitic nitrogen-containing steel component comprises nitrogen in the range of 0.03-3.0wt% following the process in step ii).
7. The process according to any one of the preceding claims, wherein the steel component, such as a core of the steel component, produced in step iii) further comprises retained austenite in an amount equal to or less than 50%.
- 15 8. The process according to any one of the preceding claims, wherein the fine-grained martensite structure component is characterised by a composition comprising:
 - a. 0.02 wt% to 3 wt% N;
 - b. 0.02 wt% to 3 wt% C; and
 - 20 c. 4.5 wt% to 30 wt% Cr.
9. The process according to any one of the preceding claims, wherein the fine-grained martensite structure component is formed from austenite grains of step iv) having a grain size of less than 50 μm .
- 25 10. The process according to any one of the preceding claims, comprising an additional step, step vi) comprising tempering the steel component at least once in the temperature range of 60°C to 700°C.
- 30 11. The process according to any one of the preceding claims, comprising a thermal treatment at least once at sub-zero Celsius temperature between step v) and step vi), such as at temperatures between -200°C to 0°C, such as -150°C to 0°C, such as -100°C to 0°C.

12. The process according to any one of the preceding claims, wherein step ii) comprises either gas nitriding or plasma nitriding.
13. The process according to any one of the preceding claims, wherein introducing nitrogen is performed using a gas mixture comprising one or more of ammonia,
5 nitrogen, hydrogen, cyanides and/or argon.
14. The process according to any one of the preceding claims, wherein step iii) is performed under vacuum.
15. The process according to any one of the preceding claims, wherein step iii) and/or step iv) is/are performed within an inert atmosphere comprising one or
10 more of the followings: nitrogen, argon and/or helium.
16. The process according to claim 15, wherein the pressure is at least 0.15 bar, preferably between 0.15 and 15 bars, more preferably between 0.25 and 15 bars.
17. The process according to any one of the preceding claims, wherein prior to step
15 iii) and/or step iv) the steel component is taken to a temperature which is below 600°C, such as below 400°C, such as below 200°C, such as below 100°C, to produce phases and/or microstructures comprising carbides and/or nitrides.
18. The process according to any one of the previous claims, wherein the
20 temperature T1 is above 1000°C, such as equal to or above 1100°C, such as equal to or above 1150°C, such as equal to or above 1200°C, with the prerequisite that the T1 is still below the melting point of the steel component.
19. The process according to any one of the previous claims, wherein the temperature T2 is below 850°C, such as equal to or below 800°C, such as equal to or below 750°C, such as equal to or below 650°C.
20. The process according to any one of the previous claims, wherein the
25 temperature T2 is in the range of 500-800°C, preferably between 600 and 750°C.
21. The process according to any one of the previous claims, wherein the
30 temperature T3 in step iv) is at a temperature below T1, such as at a temperature that does not exceed the melting point of the steel component.

22. The process according to any one of the previous claims, wherein the temperature T3 is at least 900 °C, preferably between 980 °C and 1150 °C, more preferably between 1000 °C and 1100°C.
- 5 23. The process according to any one of the previous claims, wherein steps iv) and v) are performed at a pressure between 0.15-15 bar, preferably between 0.25 and 15 bar, more preferably between 0.25 and 10 bar, more preferably between 0.36 and 4 bar.
24. The process according to any one of the previous claims, further comprising the step of applying a carburizing step or a carbo-nitriding step prior to the step ii).
- 10 25. The process according to any one of the previous claims, wherein the fine-grained martensite structure component is in the form of a case surrounding a core having a second structure component, which is different from the fine-grained martensite structure component.
- 15 26. The process according to any one of the previous claims, wherein the fine-grained martensite structure component is in the form of a case, wherein the case has a depth in the range of 0.05-30 mm, such as 0.05-20 mm, such as 0.05-10 mm.
- 20 27. A steel component comprising a fine-grained martensite structure component obtained by the process according to any one of the preceding claims 1-26, wherein the fine-grained martensite structure component is characterised by a composition comprising:
- 25 a. 0.02 wt% to 3 wt% N;
 b. 0.02 wt% to 3 wt% C; and
 c. 4.5 wt% to 30 wt% Cr,
 wherein the fine-grained martensite structure component is in the form of a case surrounding a core having a second structure component which is different from the fine-grained martensite structure component.
- 30 28. A steel component comprising a fine-grained martensite structure component, wherein the fine-grained martensite structure component is in the form of a case surrounding a core having a second structure component, wherein the core and the case are different, and further wherein the fine-grained martensite structure component is characterised by a composition comprising

- a. 0.02 wt% to 3 wt% N;
 - b. 0.02 wt% to 3 wt% C; and
 - c. 4.5 wt% to 30 wt% Cr.
- 5 29. The steel component according to claim 28, wherein the steel component comprises at least an amount of carbon- and/or nitrogen-containing precipitates.
30. The steel component according to claim 29, wherein the nitrogen level in the core is lower than the nitrogen level in the case.
- 10 31. The steel component according claims 28-30, wherein the fine-grained martensite structure component has a hardness in the range of 300-1400 HV1.
32. The steel component according to claims 28-31, wherein the fine-grained martensite structure component is formed from austenite grains, wherein the austenite grains, prior to transformation into the fine-grained martensite structure component, have a grain size of less than 50 μm .
- 15 33. The steel component according to claims 28-32, wherein the case has a depth in the range of 0.05-30 mm, such as 0.05-20 mm, such as 0.05 to 10 mm.
34. The steel component according claims 28-33, wherein the fine-grained martensite structure component and/or the second structure component is/are not identical to SAE AMS 5898.
- 20 35. The steel component according to claims 28-34, further comprising at least one other alloying elements.
36. The steel component according to claims 28-35, wherein the at least one alloying elements are one or more selected from Si, Mo, Mn, Nb, V, Ta, Ti, Ni, Cu and Co.
- 25 37. A steel component according to any one of claims 27-36 for use in bearings, gears, crankshafts, screws, tools, weapons, armours, knives, medical and/or dental utensils.
38. A steel component according to any one of claims 27-36 for use in wind turbine components.

39. A steel component according to any one of claims 27-36 for use preventing white etching cracks in bearings.

40. A steel component according to any one of claims 27-36 for use in and/or for prevention of rolling and/or sliding contact fatigue.

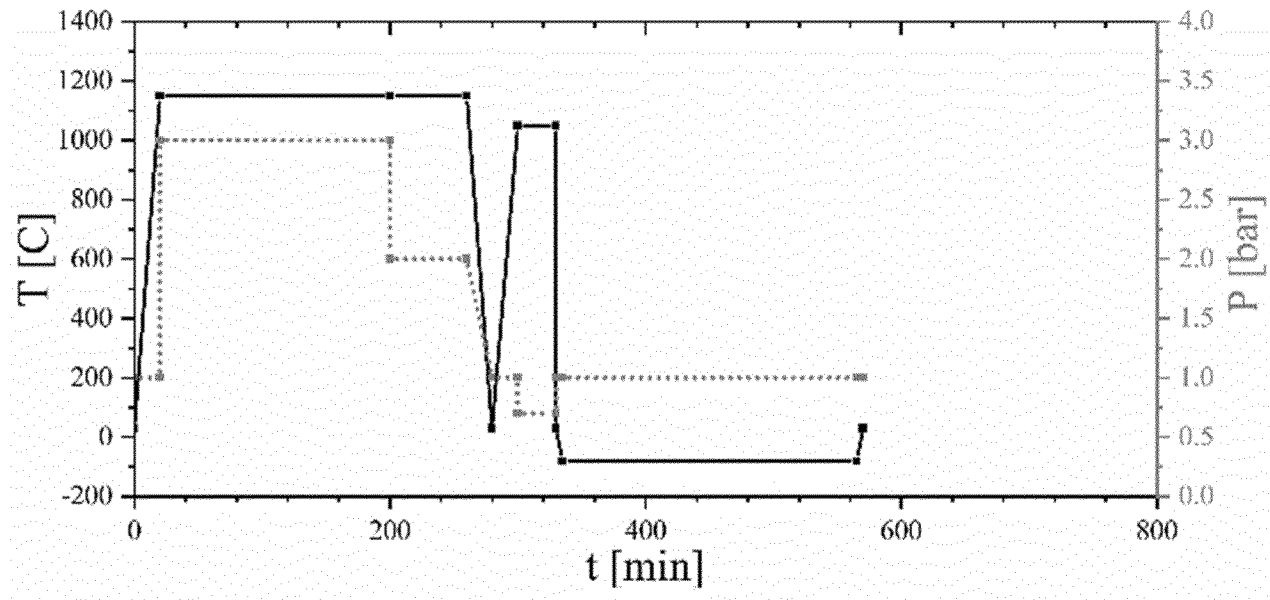


Fig. 1a

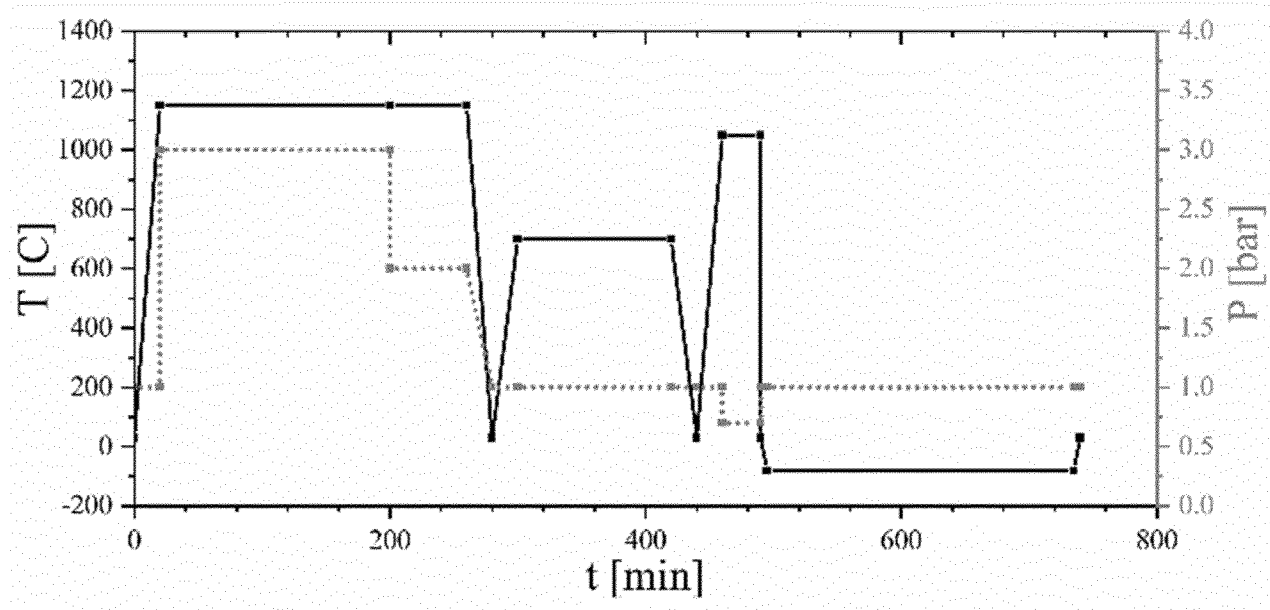


Fig. 1b

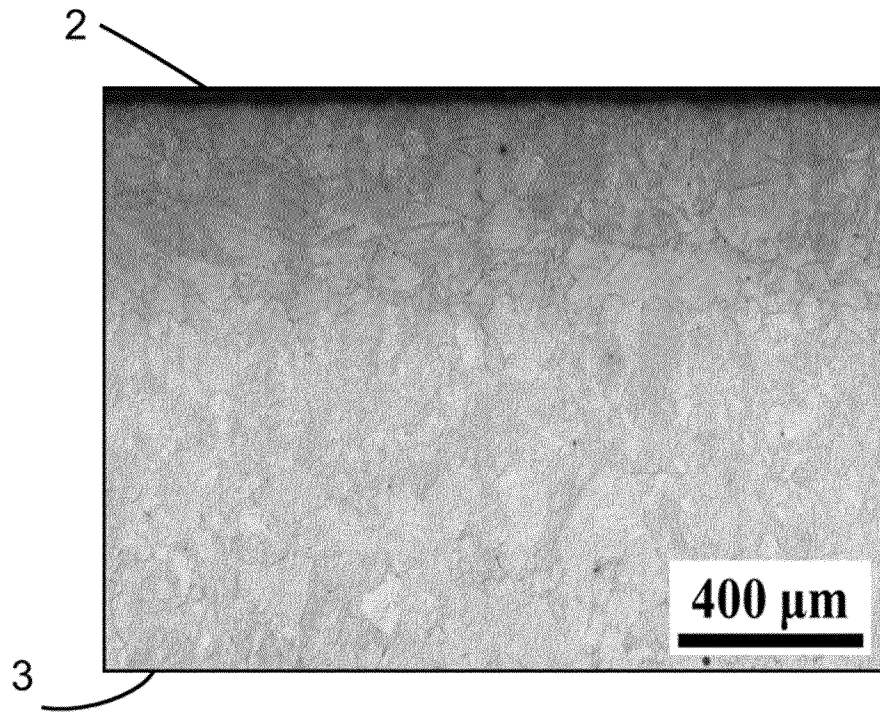


Fig. 2a

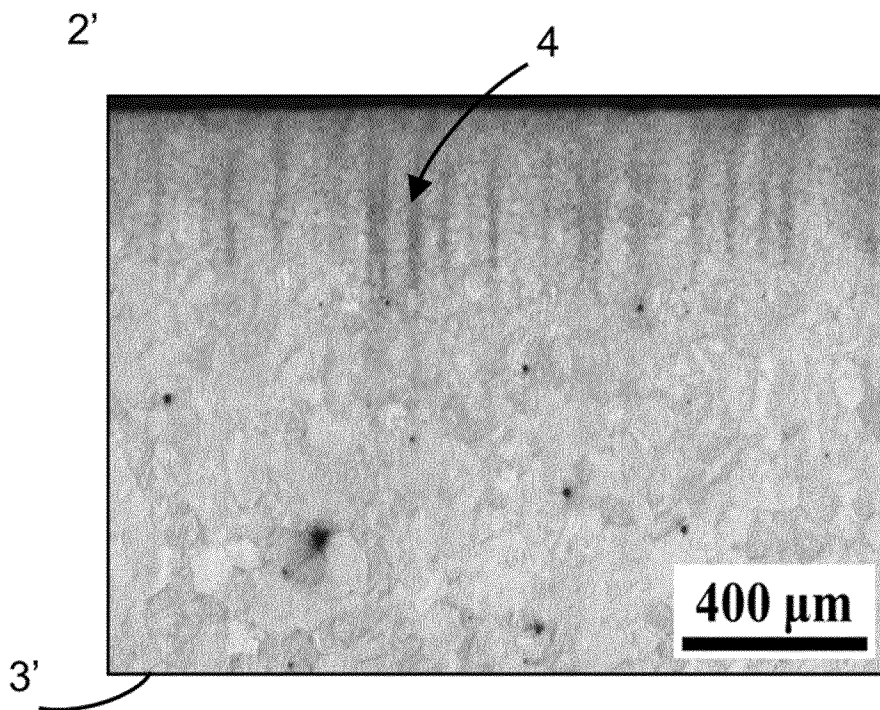


Fig. 2b

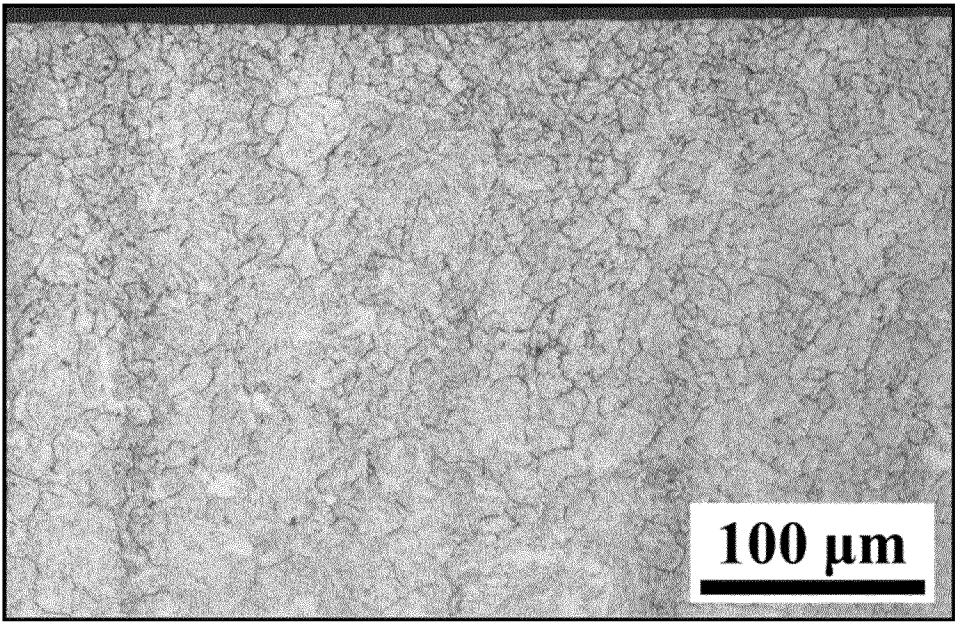


Fig. 3

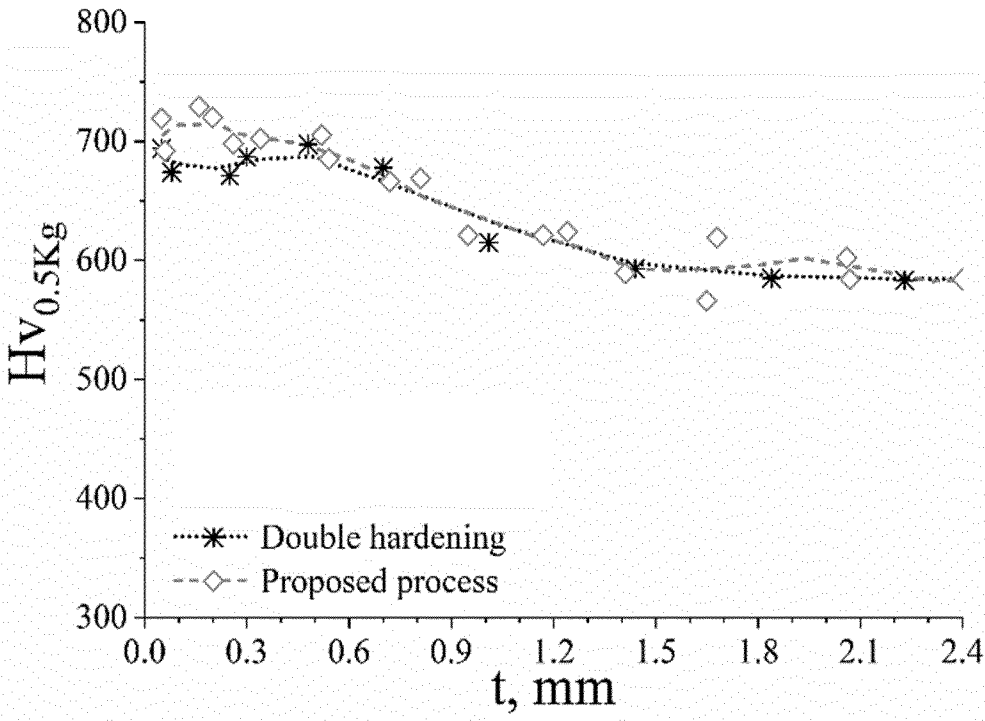


Fig. 4

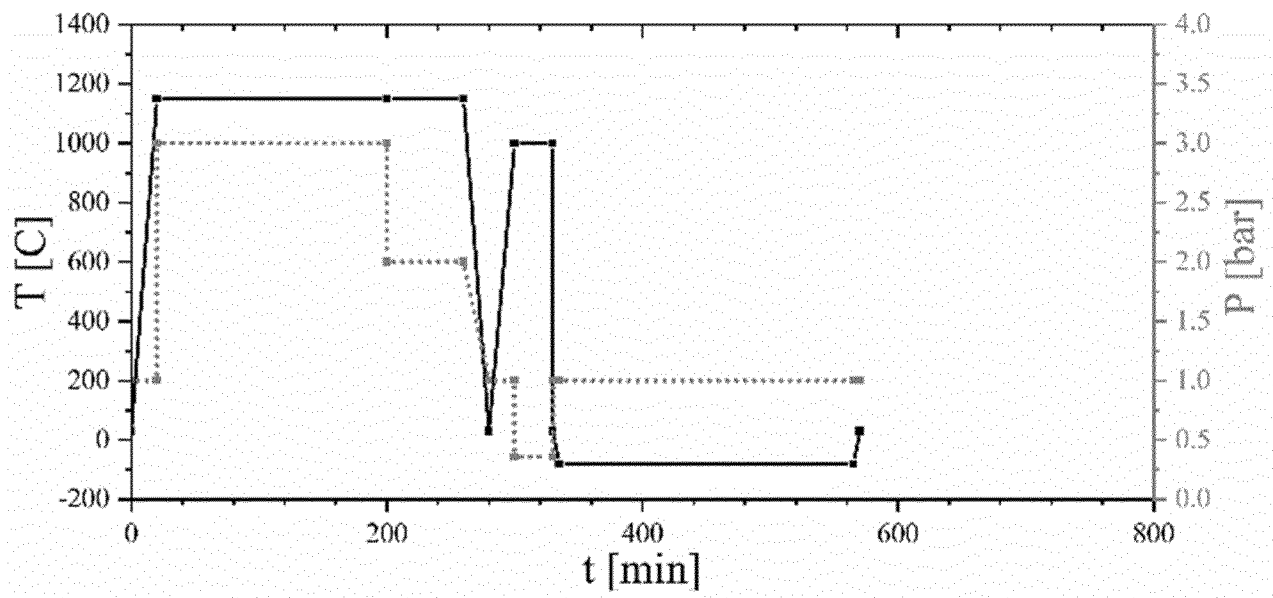


Fig. 5a

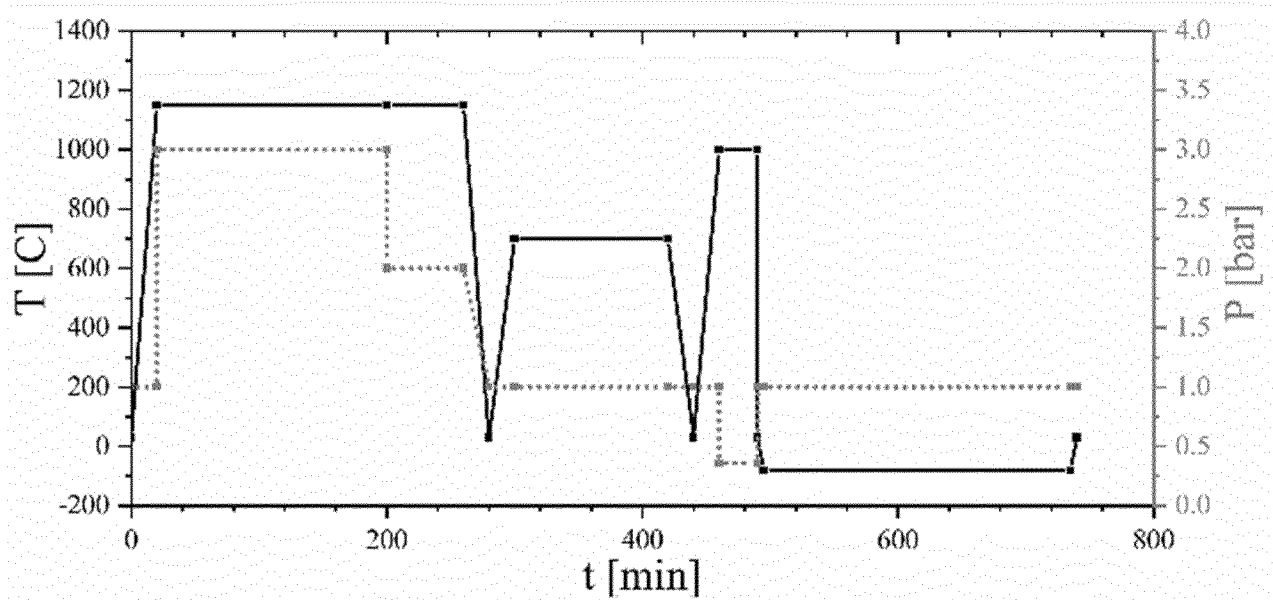


Fig. 5b

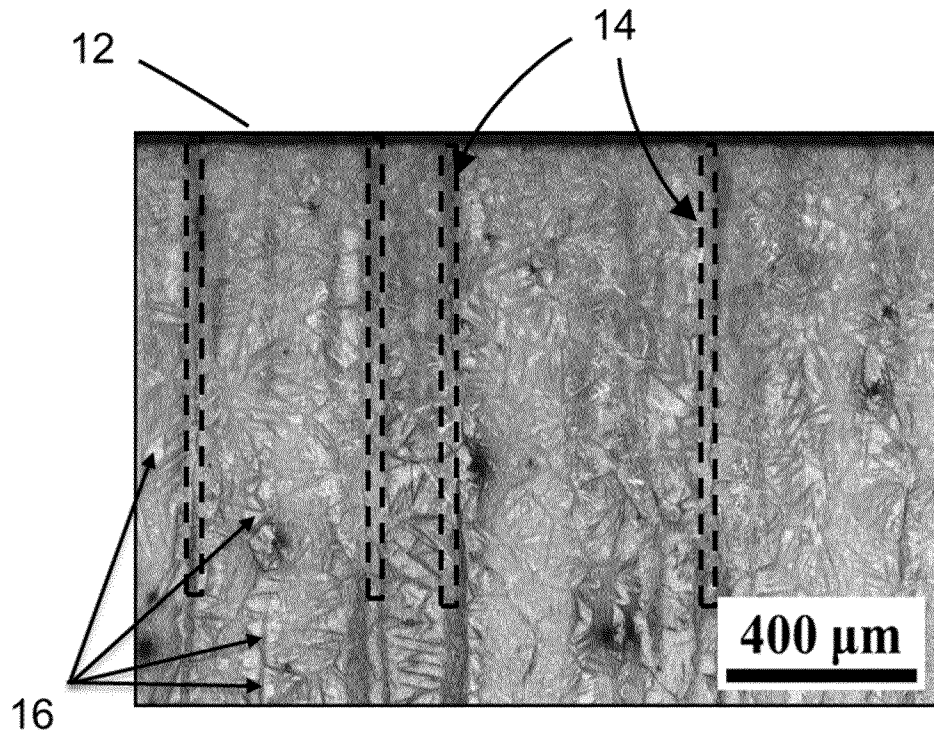


Fig. 6a

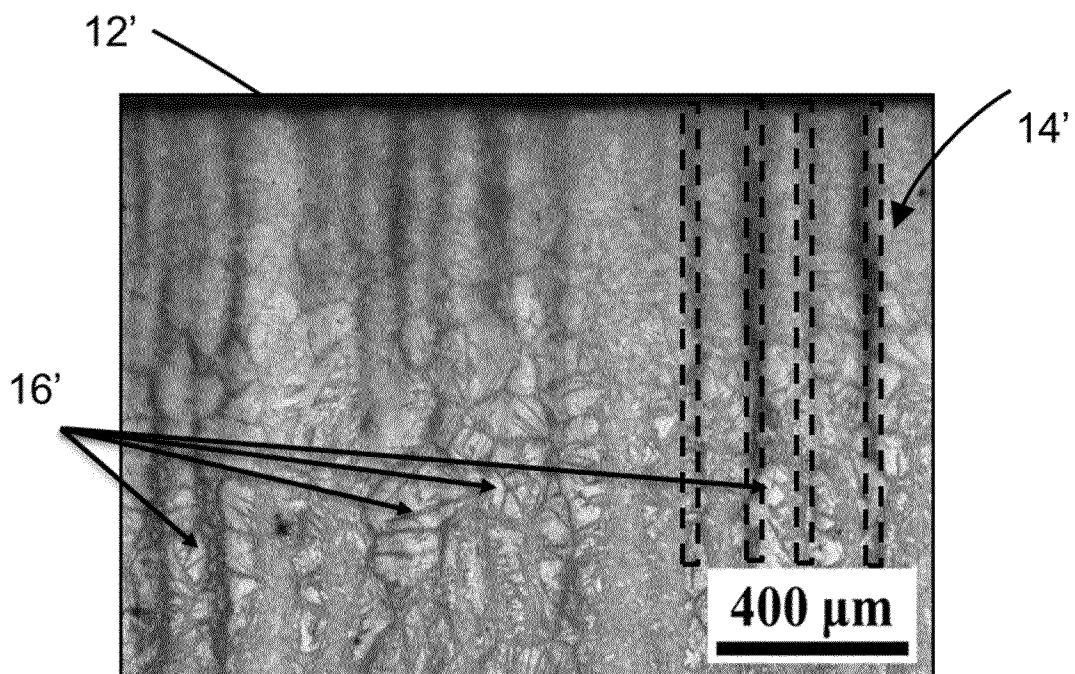


Fig. 6b

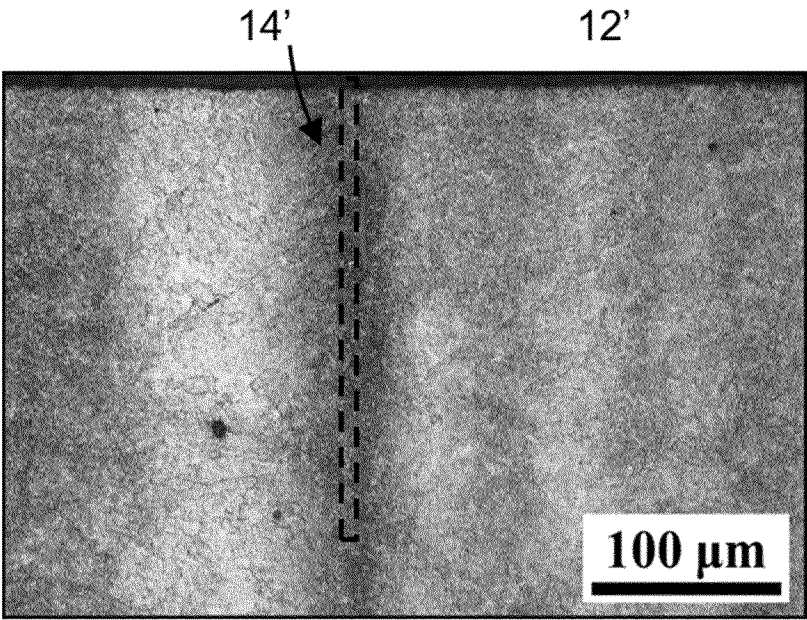


Fig. 7

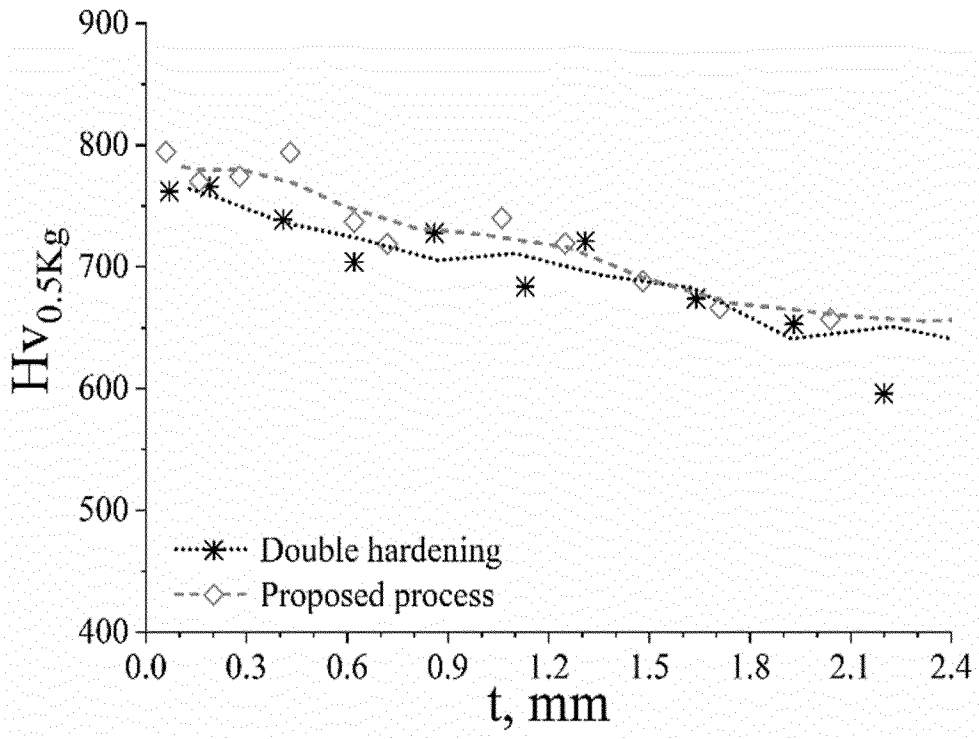


Fig. 8

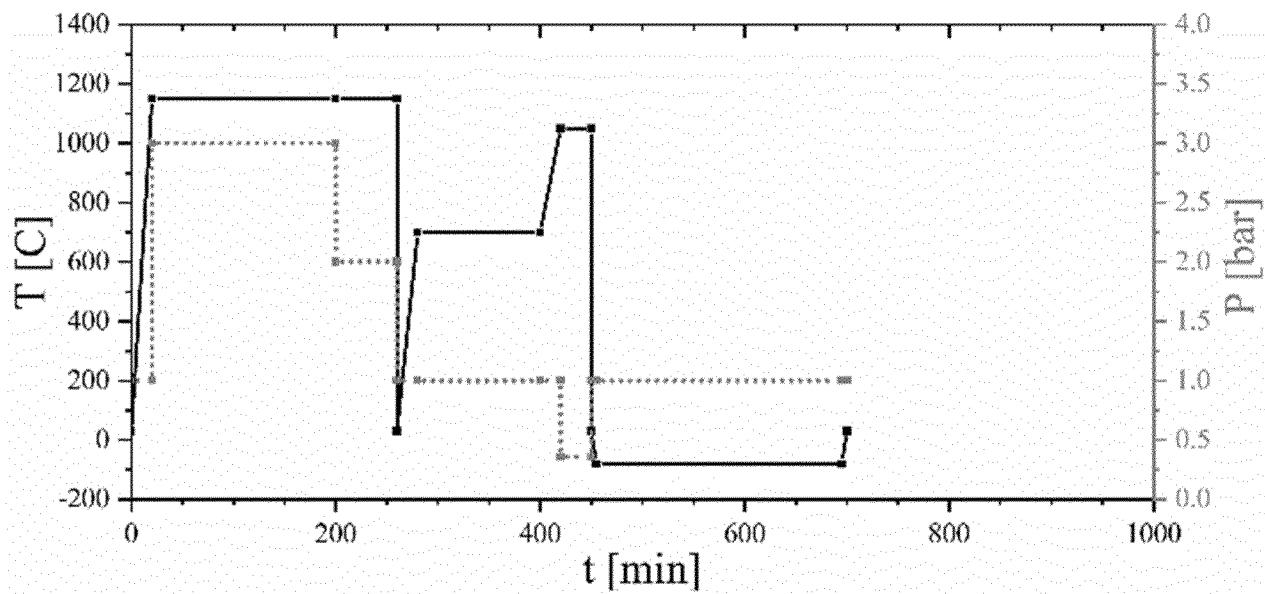


Fig. 9a

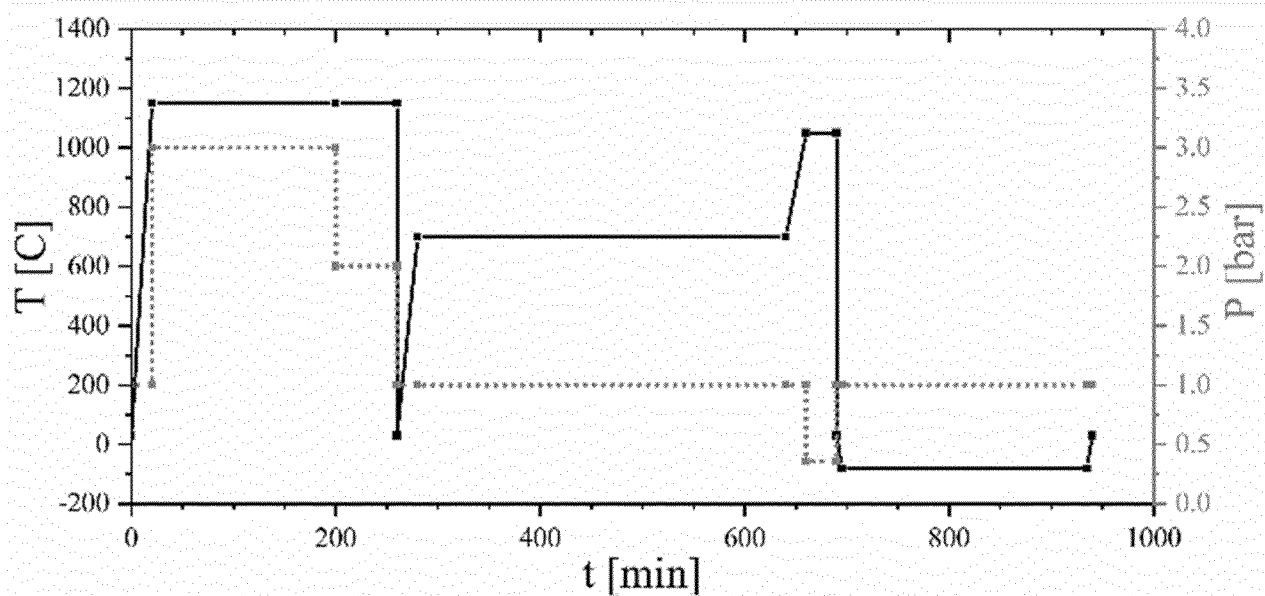


Fig. 9b

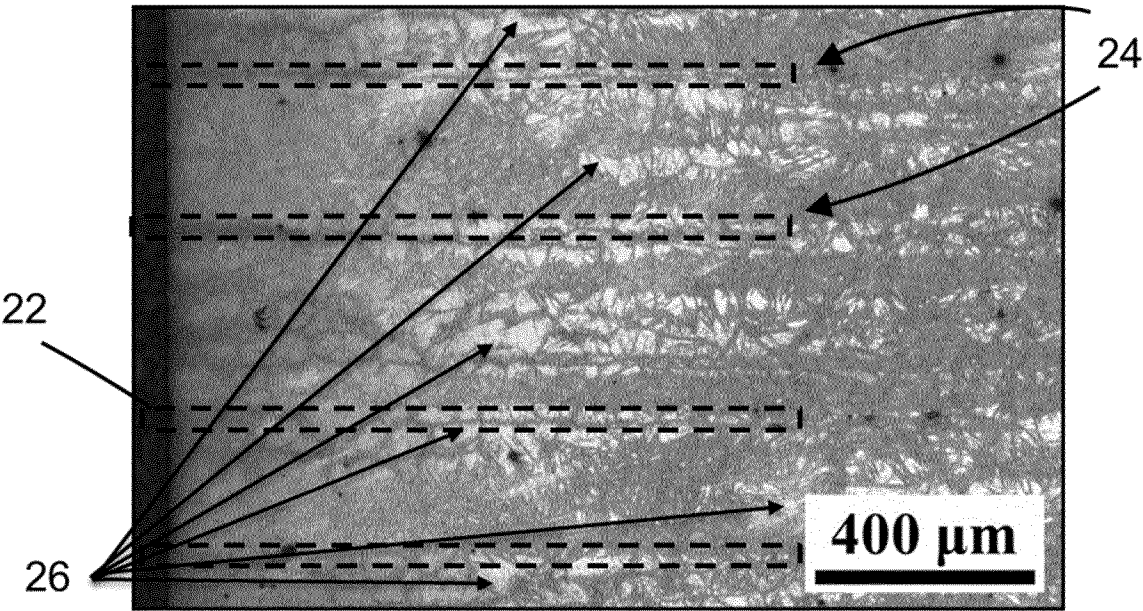


Fig. 10a

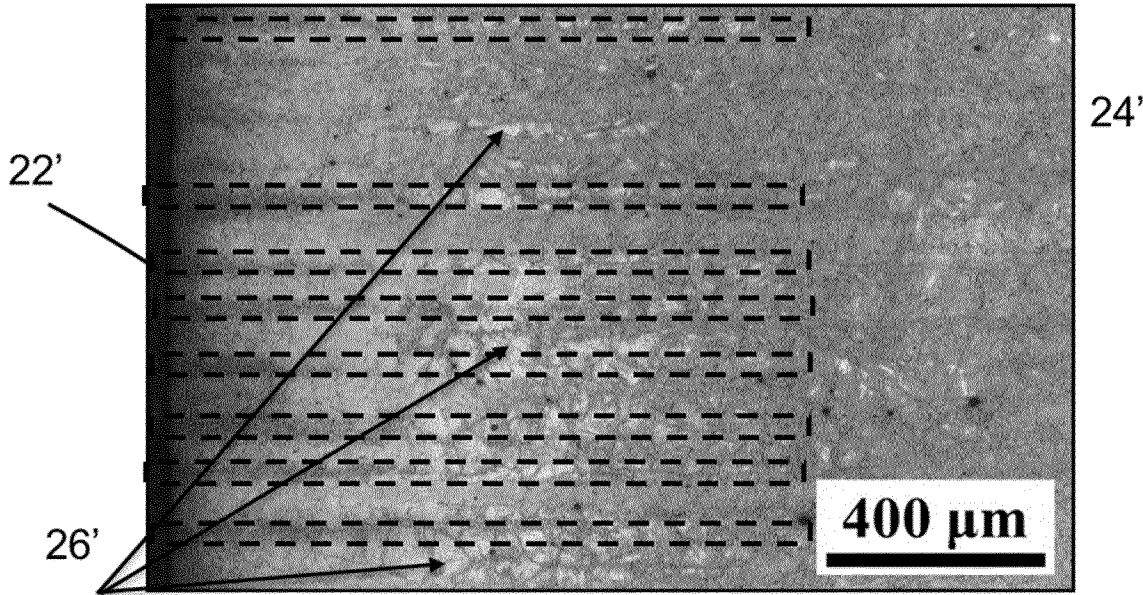


Fig. 10b

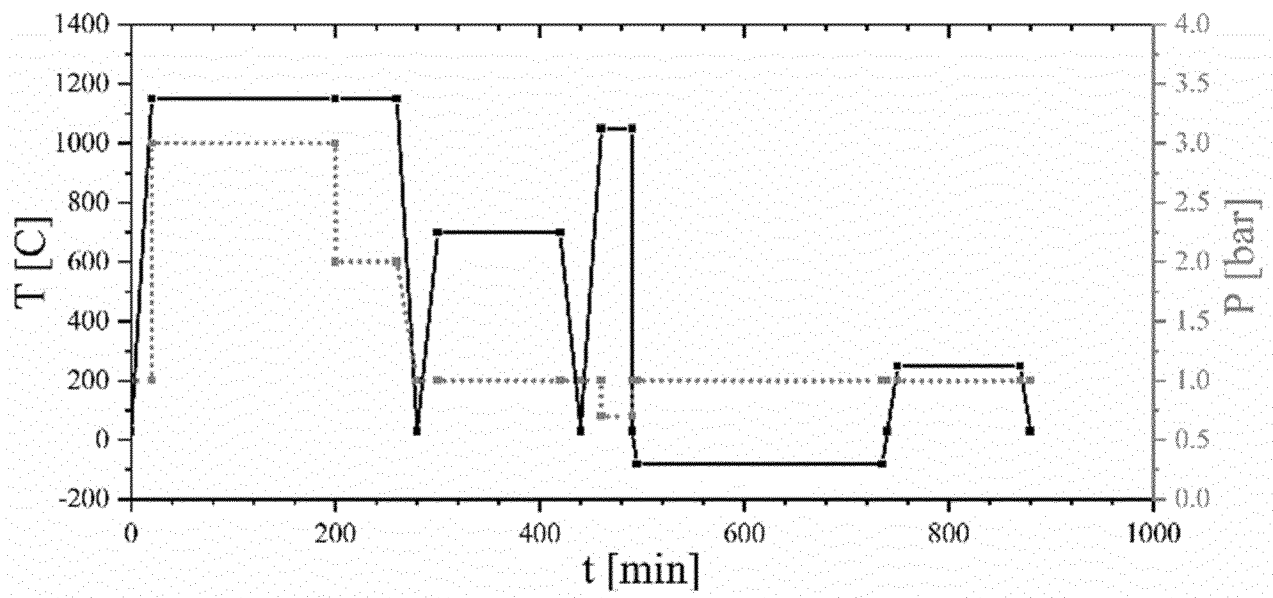


Fig. 11

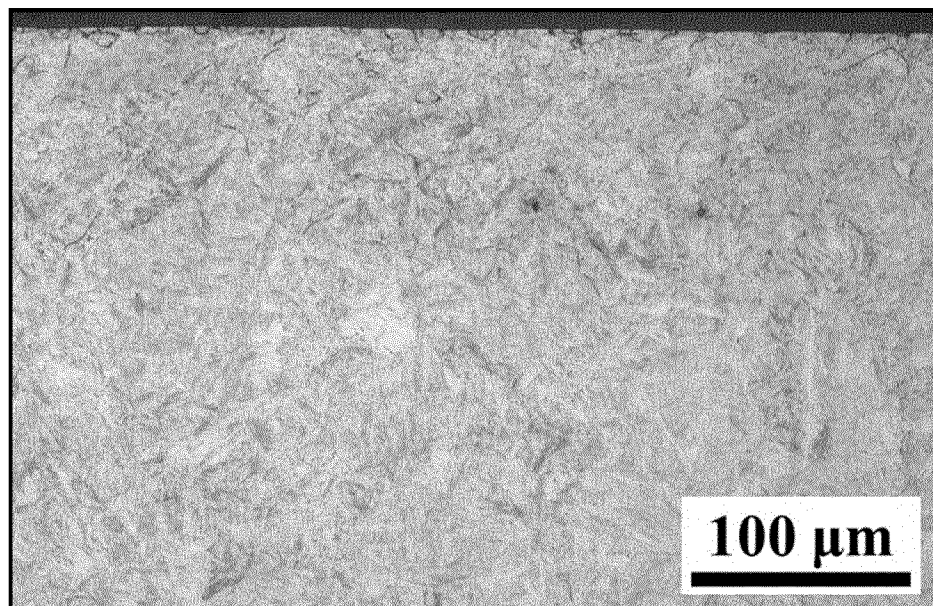


Fig. 12

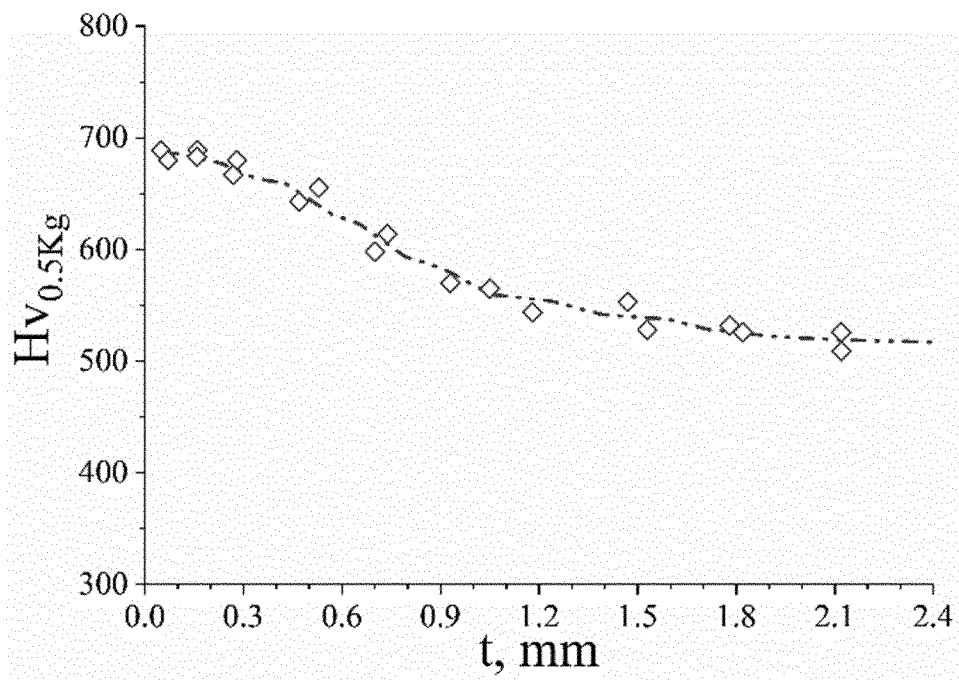


Fig. 13

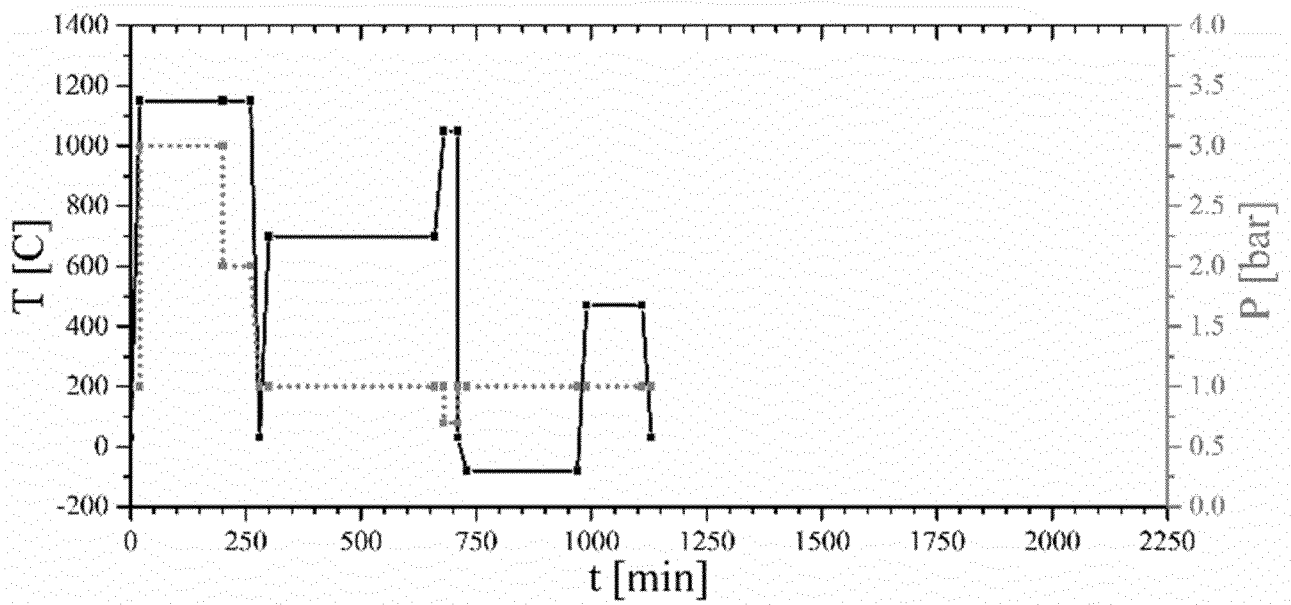


Fig. 14

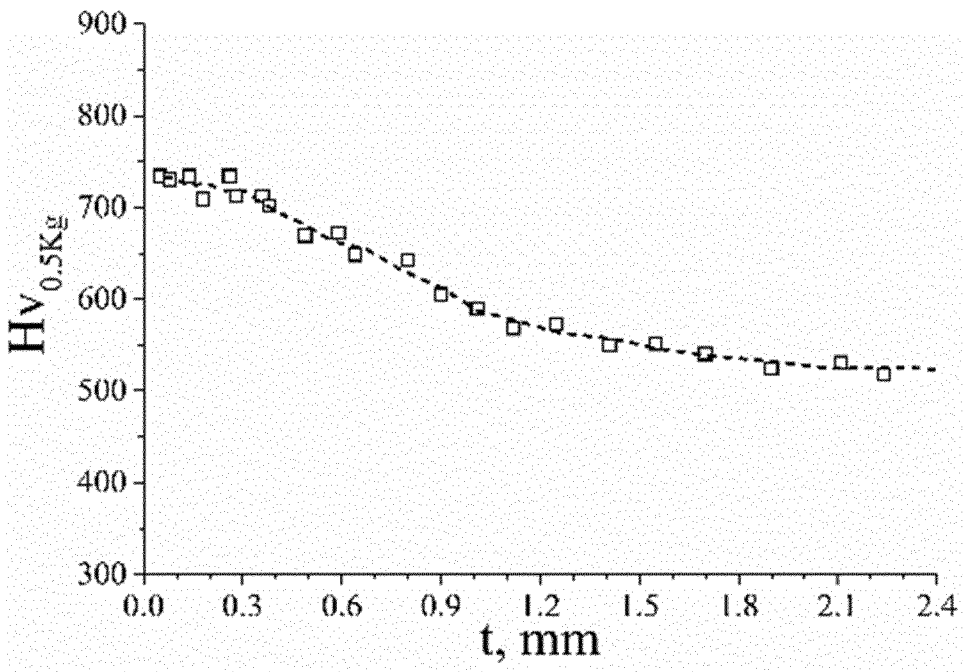


Fig. 15

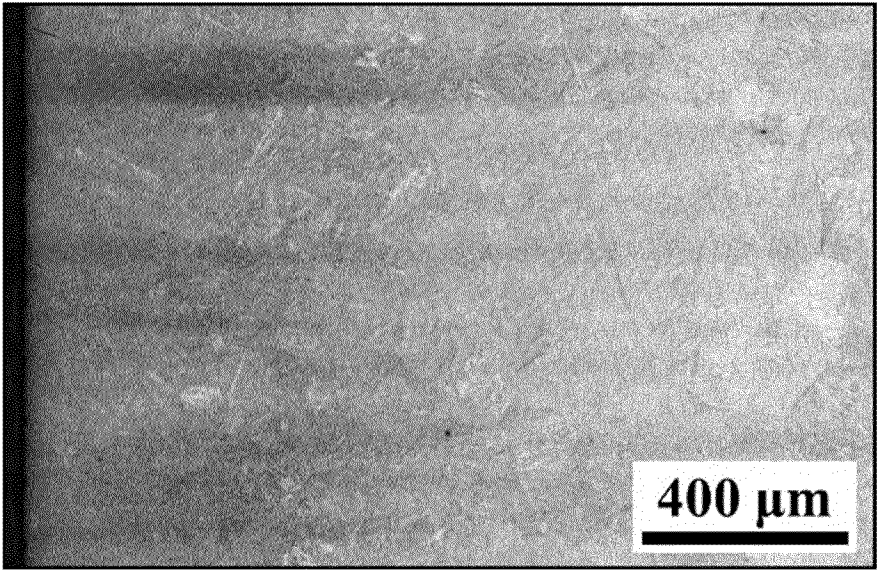


Fig. 16

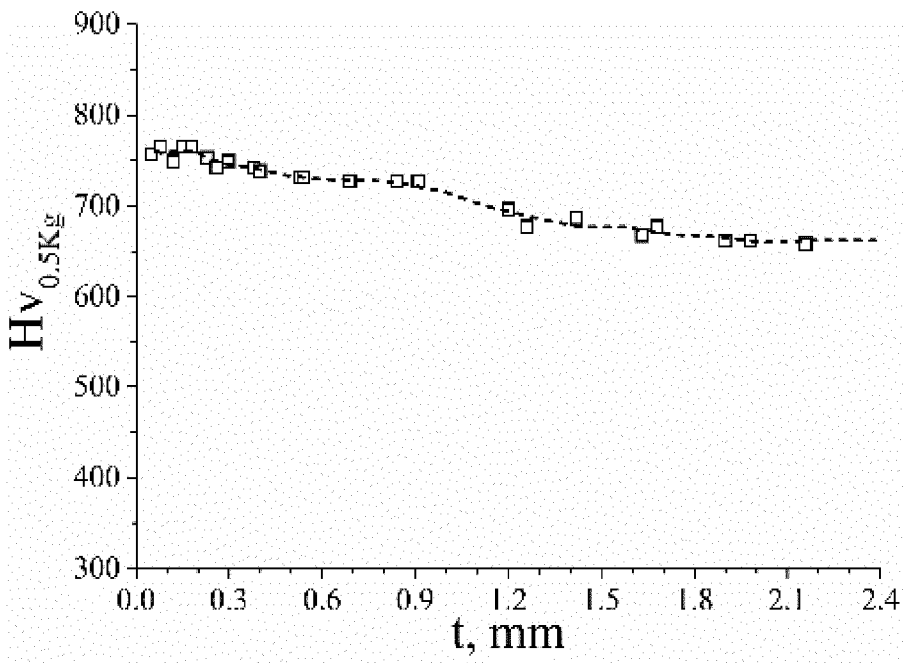


Fig. 17

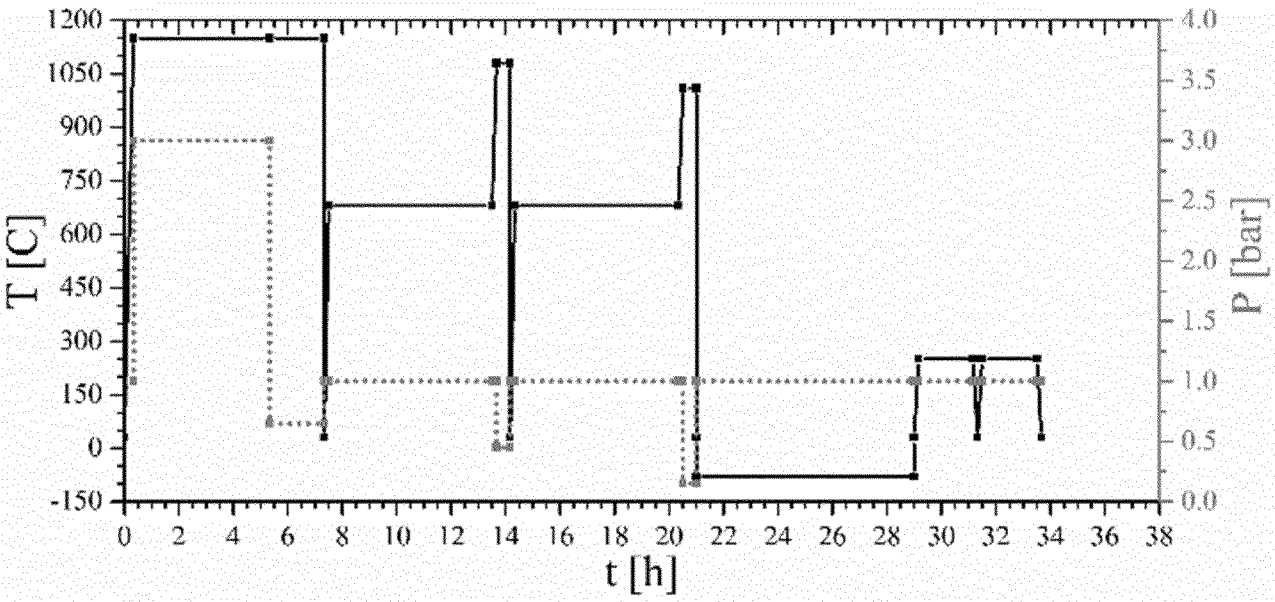


Fig. 18

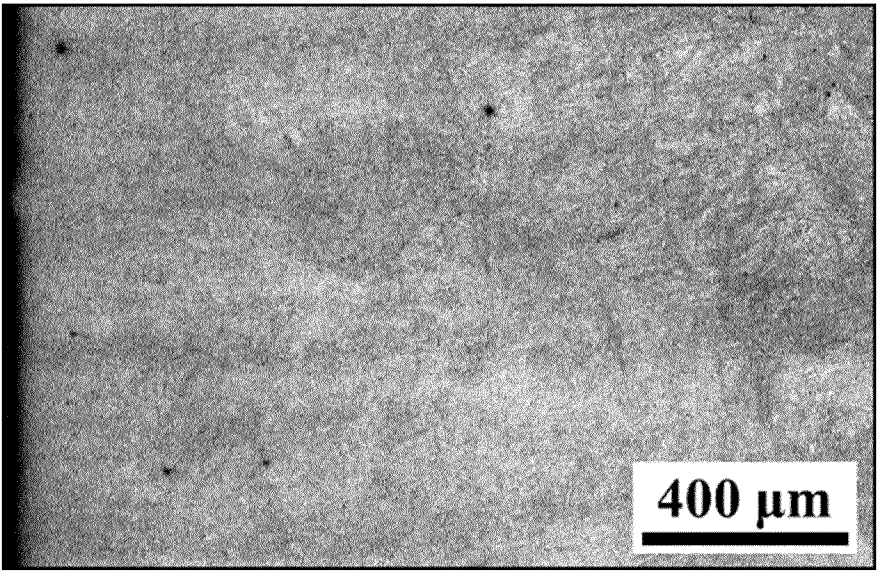


Fig. 19

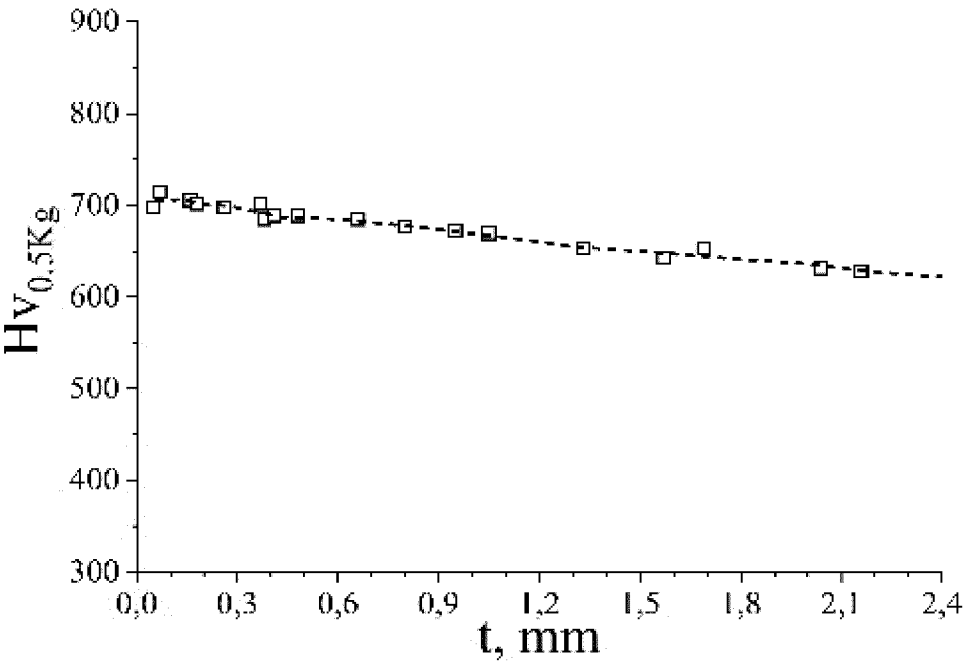


Fig. 20

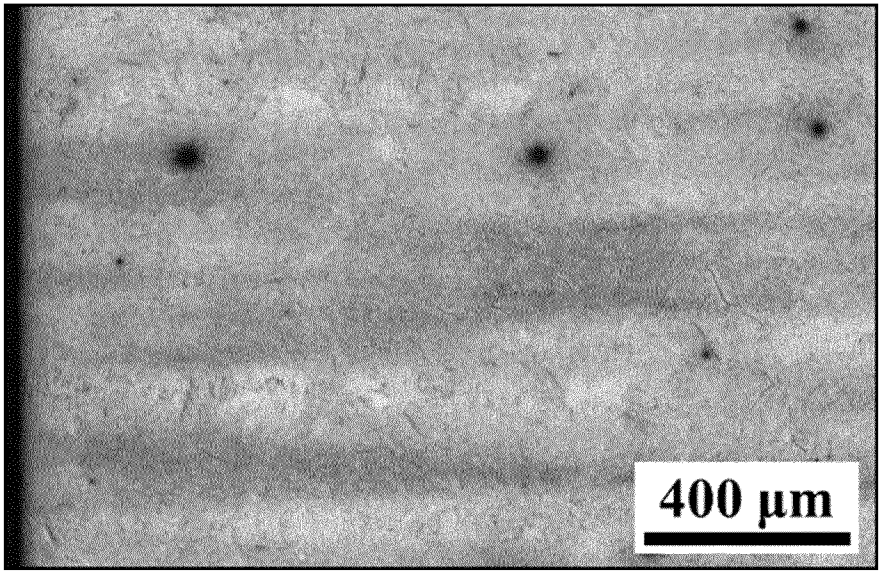


Fig. 21

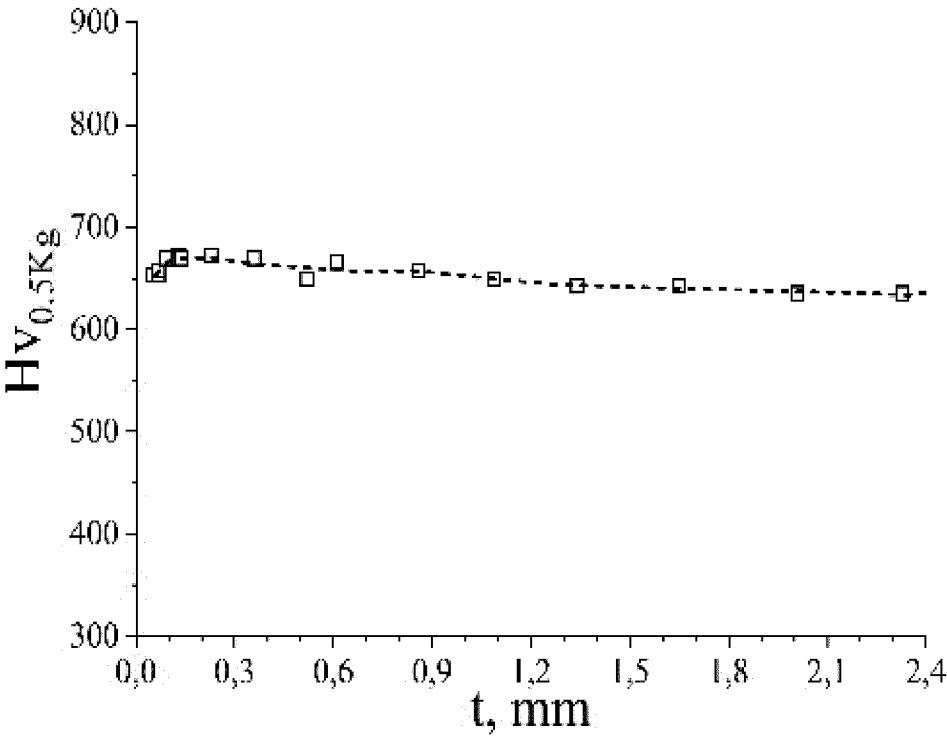


Fig. 22

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2022/069001

A. CLASSIFICATION OF SUBJECT MATTER INV. C21D1/06 C21D1/18 C21D1/25 C21D1/26 C21D1/76 C21D6/00 C21D6/04 C21D8/06 C21D8/10 C21D9/00 C21D9/18 C21D9/22 C21D9/32 C21D9/38 C21D9/40				
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) C21D 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.		
X	JP 2015 232164 A (NSK LTD) 24 December 2015 (2015-12-24) 0001, 0021; tab. 1, 4; tab. 4, 4; fig. 2, 3 -----	1-40		
X	JP 2020 180313 A (DAIDO STEEL CO LTD) 5 November 2020 (2020-11-05) 0049-0057, 0070; tab. 1-3; fig. 1 -----	1-40		
X	EP 3 536 812 A1 (HILTI AG [LI]) 11 September 2019 (2019-09-11) 0001, 0017, 0018, 0022, 0023, 0025, 0028; cl. 1-10 -----	1-40		
X	EP 2 888 377 A1 (SKF AB [SE]) 1 July 2015 (2015-07-01) 0003, 0024, 0025, 0028, 0034; fig. 1, 2 ----- -/--	1, 6-13, 15-28		
<div style="display: flex; justify-content: space-between;"> <div> <input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. </div> <div> <input checked="" type="checkbox"/> See patent family annex. </div> </div>				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents :</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"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</p> <p>"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</p> <p>"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</p> <p>"&" document member of the same patent family</p> </div> </div>				
Date of the actual completion of the international search <div style="text-align: center;">28 September 2022</div>		Date of mailing of the international search report <div style="text-align: center;">10/10/2022</div>		
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 <div style="text-align: center;">Kreutzer, Ingo</div>		

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2022/069001

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>BERTON ELISIANE MARIA ET AL: "Quenching and tempering effect on the corrosion resistance of nitrogen martensitic layer produced by SHTPN on AISI 409 steel", SURFACE AND COATINGS TECHNOLOGY, ELSEVIER, NL, vol. 395, 16 May 2020 (2020-05-16), XP086168425, ISSN: 0257-8972, DOI: 10.1016/J.SURFCOAT.2020.125921 [retrieved on 2020-05-16] p. 1+2; tab. 1, 2; fig. 1, 3</p> <p>-----</p>	<p>1-4, 6-10, 12-23, 25-36</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2022/069001

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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JP 2020180313 A	05-11-2020	NONE	
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