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AND USE THEREOF, IN PARTICULAR FOR
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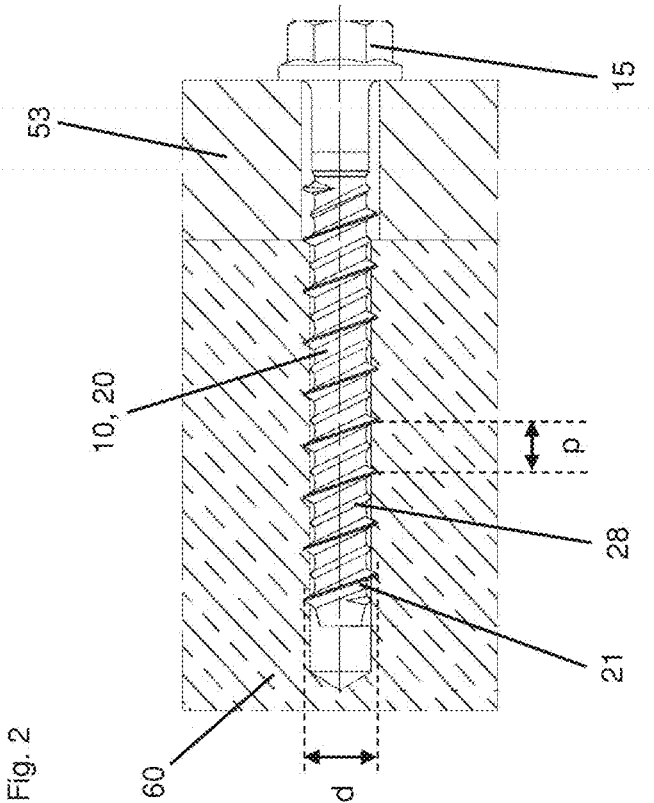
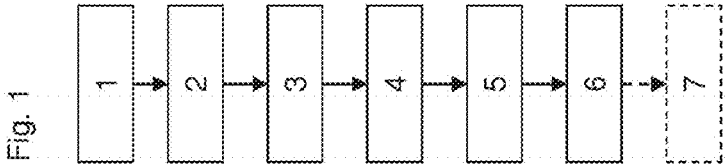
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ABSTRACTA steel comprising 0.07 to 0.14 wt. % of carbon, 13 to 15 wt.
% of chromium, 1.3 to 1.7 wt. % of molybdenum, 1.5 to 2.0
wt. % of nickel and 1.0 to 1.5 wt. % of manganese and use
of the steel for producing screws is provided.



MARTENSITICALLY HARDENABLE STEEL AND USE THEREOF, IN PARTICULAR FOR PRODUCING A SCREW

[0001] The invention relates to a method for producing a shaped body, in particular a hardened shaped body, from a blank, a steel, its use for producing a screw, and a screw.

[0002] Desirable for concrete screws and self-tapping screws used in steel-metal applications are material concepts with high surface hardness (at least in some areas of the screw), high core toughness, high resistance to general corrosion, pitting corrosion, as well as chloride or hydrogen-induced embrittlement and good plastic formability. According to EP 2204244 A1 and the concrete screws which are offered under the name "Hilti HUS-HR", this is achieved by carbide cutting elements, which are welded in the tip region of the screw on the screw thread, with the screw otherwise made of austenitic stainless A4 steel, comparable to 1.4401. However, such screws can be relatively expensive to manufacture.

[0003] In the field of stainless self-tapping screws for steel-metal applications, so-called bimetallic screws are known, which are characterized in that a bolt made of hardenable carbon steel is welded on the screw body, i.e. on the head and the shaft, which are made of austenitic stainless A2 or A4 steel (comparable to 1.4301 or 1.4401). This bolt is hardened after welding and forming by means of a local heat treatment. Even such screws can be relatively expensive to manufacture.

[0004] DE4033706 A1 describes a heat treatment method for increasing the corrosion resistance of a hardened edge layer of near net-shaped components made of martensitic stainless steels with less than 0.4 wt % carbon, by diffusion of 0.2 to 0.8 wt % nitrogen into the edge layer. However, an application in screws is not taught by DE4033706A1 and, more particularly, DE4033706A1 is not concerned with tuning the chemical composition of the steel and the heat treatment parameters for use in screws.

[0005] DE19626833A1 describes a method for producing a highly corrosion-resistant martensitic edge layer over a ferritic-martensitic core in components made of stainless steel. The chemical composition of the steel is limited so that there is a ferritic-martensitic structure and, after case-hardening at a temperature of 1,050° C.-1,150° C. with nitrogen, the ferrite content in the core is between 40 and 90 vol %, and the core hardness is less than 300 HV30. Once again, an application of the method for screws is not taught.

[0006] DE1 0201 3 10801 8 A1 describes a screw made of a stainless steel, for example, 1.41 13, wherein the steel is substantially free of nickel, wherein, due to a nitriding heat treatment at 1,000-1,200° C., an edge layer has a dissolved nitrogen content which is elevated compared to the rest of the structure, and wherein the screw in the edge layer has a martensitic structure and otherwise a ferritic structure.

[0007] WO1 4040995 A1 describes a method for producing a self-tapping concrete screw in which a blank of a martensitically hardenable steel, in particular with a carbon content less than 0.07%, is hardened at a temperature greater than 900° C. in a nitrogenous gas atmosphere.

[0008] TW201418549 A describes a screw with a steel comprising 0.26 to 0.40% carbon, 12 to 14% chromium, 0 to 0.6% nickel, and 0 to 1% manganese.

[0009] The summary retrievable under the link: https://online.unileoben.ac.at/mu_online/wbAbs.showThesis?pThesisNr=61746&pOrgNr=1 indicates that

martensitic steels, edge-nitrided with the high temperature gas-nitriding process and comprising 14% chromium, may be particularly suitable for use as a material for a fastening element.

[0010] The object of the invention is to provide a method for producing a shaped body, in particular a screw shape, from a steel blank and a corresponding steel, with which at particularly low production costs and with a high product reliability, especially for screw applications, a particularly advantageous combination of surface hardness, core toughness and corrosion resistance, resistance to hydrogen- and chloride-induced embrittlement and workability, in particular formability, can be realized. Another object of the invention is to provide a use of such a steel and a screw comprising such a steel, with which the aforementioned advantages can be implemented.

[0011] The object is achieved according to the invention by a method having the features of claim 1, a steel having the features of claim 8, the use thereof for producing a screw according to claim 9, and a screw according to claim 10. Preferred embodiments are indicated in the dependent claims.

[0012] A method according to the invention is used to produce a shaped body, preferably a screw shape, and uses a blank comprising a steel with a weight fraction of 0.07 to 0.14 wt % carbon, 13 to 15 wt % chromium, 1.3 to 1.7 wt % molybdenum, 1.5 to 2.0 wt % nickel and 1.0 to 1.5 wt % manganese. In addition, the steel may have other admixtures customary in steel, for example vanadium (in particular <0.2 wt %), niobium (in particular <0.2 wt %), titanium (in particular <0.2 wt %) and/or silicon (in particular <0.5 wt %). The remainder is iron with unavoidable impurities, for example sulfur and/or phosphorus, in particular <0.02% by weight in each case. Statements to the effect of "wt %" can be understood in the usual way as percentages by weight. In particular, the steel may be referred to as a martensitically hardenable stainless steel. Preferably, the steel has a weight proportion of 0.08 to 0.12% carbon by weight.

[0013] The invention is based on the recognition that stainless martensitic steels can be promising candidates to meet the in part conflicting requirements of steel that may arise when it is used in screws, especially in self-tapping screws. In order to meet the diverse requirements of high surface hardness and sufficient hardness penetration depth, good corrosion resistance, good toughness and high resistance to chloride- or hydrogen-induced embrittlement, the chemical composition of the steel (in particular with regard to the alloy constituents carbon, chromium, molybdenum, nickel and manganese) and the multi-stage heat treatment required for the adjustment of the property profile consisting of high-temperature gas-nitriding, gas phase quenching, low-temperature cooling, annealing and optional local induction hardening must be carefully coordinated. Previous concepts according to the prior art are often based on a combination of a chemical composition of the stainless martensitic steel and a heat treatment that is rather unfavorable for a screw, so that often not all properties required for a screw can be sufficiently met at the same time.

[0014] Normally, the achievable hardness of martensitic stainless steels primarily depends on the carbon content, as in classic tempered steels. As the carbon content increases, the hardness increases, but with higher sensitivity to hydrogen embrittlement and less toughness. For this reason, steels comparable to 1.4108 are generally unsuitable for use in

screws under corrosive conditions. Such nitrogen-alloyed steels comprising a carbon content of 0.25-0.35 wt % have a sufficiently high surface hardness and a good resistance to pitting corrosion, but are regularly very brittle and relatively sensitive to hydrogen embrittlement.

[0015] In soft-martensitic steels, the carbon content is lowered (<0.1 wt % C) and replaced by austenite-stabilizing nickel. As a result, an extreme toughness, but at the same time a slightly lower hardness compared with martensites with higher carbon content, is achieved as a rule. The steel grade 1.4313 (X3CrNiMo13-4) is a representative of the soft-martensitic steel group. In addition, this type of stainless martensitic steels is often suitable for use in screws only to a limited extent at best, because the steels often have only a relatively low surface hardness and often have a corrosion resistance that is still too low for a screw application.

[0016] Stainless martensitic steels offer the option of setting the required combination of high edge hardness with simultaneously lower core hardness (equivalent to good toughness and high resistance to chloride- or hydrogen-induced embrittlement) and good corrosion resistance by case-hardening with nitrogen instead of carbon. Nitrogen, which is dissolved in the component during a case-hardening process of this kind, increases the surface hardness, the corrosion resistance, and the compressive residual stress of the edge layer. Due to the nitrogen dissolved in the surface layer of the component, this heat treatment method is also referred to as "solution nitriding".

[0017] The invention includes a steel, the chemical composition of which is based on a combination of the alloying constituents carbon (0.07-0.14% by weight, preferably 0.08-0.12% by weight), chromium (13-15% by weight), molybdenum (1.3-1.7% by weight), nickel (1.5-2.0% by weight) and manganese (1.0 to 1.5%, preferably 1.2% by weight).

[0018] In the context of the invention, it has been recognized that with such a steel, in particular in connection with a heat treatment matched to the steel (preferably a multi-stage heat treatment) a particularly advantageous property profile for screws can be obtained, but in principle also for other components. As explained in detail below, this may be due in particular to austenitization with structure stabilization by delta ferrite content during the heat treatment. In particular, a property profile could be realized, which is characterized by a good formability of the blank, a high surface hardness of 580 HV0.3 or higher, a maximum core hardness of 450 HV0.3 or less, a high resistance to general corrosion and pitting corrosion in the core (represented by a PRE index of 17 or higher) and in the periphery (represented by a PRE index of 23 or higher), high core toughness (particularly as a result of a combination of low carbon content and stable delta ferrite, whereby increasing coarse grain growth is suppressed in the heat treatment) and a high resistance to chloride- or hydrogen-induced embrittlement. Specifically, the steel may be advantageous in particular in the following respect:

[0019] Due to the carbon content of the steel, the core hardness is 450 HV0.3 or less.

[0020] Due to the carbon, chromium, molybdenum, nickel and manganese content, the following will result:

[0021] A relatively high PRE Index (Pitting Resistance Equivalent), preferably 17 or higher, can be achieved, but without leaving the state range of a martensitic or martensitic-ferritic structure.

[0022] The steel has good processability into semi-finished forms such as rolled wire or drawn bare wire. Both rolled and bare wire have good cold workability, preferably represented by a yield strength R_p $0.2 < 650$ N/mm², which may be particularly advantageous for the production of screws in a cold-forming process, preferably with a rolling process.

[0023] For case-hardening in the temperature range between 1,000° C. and 1,150° C., preferably between 1,030° C. and 1,100° C., a predominantly austenitic structure (preferably between 70% and 95%) with a small proportion of delta ferrite particles may occur in the core region of the blank with a ferrite delta in the amount of 5%-30%, wherein this delta ferrite content of 5%-30% can have a stabilizing effect on the structure at said temperatures and thereby counteract grain coarsening, which can have an advantageous effect on the toughness properties. The delta ferrite content may be deliberately limited to a maximum of 30%, since at higher delta ferrite levels toughness could decrease again. The austenitic proportion of 70%-95% has high carbon solubility, effectively counteracting the formation of chromium carbides and the associated relatively high susceptibility to intergranular corrosion. Preferably, a delta ferrite content between 10% and 15% can be provided, corresponding to an austenite content between 90% and 85%.

[0024] When case-hardening in the aforementioned temperature range with diffusion of nitrogen, a mainly austenitic structure which has a high solubility of carbon and nitrogen can occur in the edge zone of the blank, so that the formation of chromium carbides or chromium nitrides and the associated relatively high susceptibility to intercrystalline corrosion is efficiently counteracted.

[0025] After the heat treatment, a mainly martensitic structure with a small proportion of delta ferrite in the amount of 5%-30% (preferably 10%-15%) can be present in the core region of the blank. The delta ferrite content may be deliberately limited to a maximum of 30%, since at higher delta ferrite levels toughness could decrease again.

[0026] After the heat treatment, a mainly martensitic structure can be present in the edge zone of the blank, so that a high degree of hardening can be achieved.

[0027] Advantageously, in the method according to the invention, the step of case-hardening the blank with nitrogen from the gas phase is provided, preferably at temperatures between 1,000° C. and 1,150° C., more preferably between 1,030° C. and 1,100° C., and/or a nitrogen partial pressure between 0.05 bar and 0.3 bar, particularly preferably between 0.10 bar and 0.20 bar, preferably following the step of processing the blank. Through such case-hardening with nitrogen (alone or, as explained below, optionally in combination with carbon), the boundary zone of the blank can be selectively modified in a particularly advantageous manner for screw application. In particular, during case-hardening between 1,000 and 1,150° C., nitrogen can be dissolved in the boundary zone of the then austenitic basic structure. In connection with the steel according to the invention, such a case-hardening made it possible to achieve a surface hardness of 580 HV0.3 or higher with a limit hardness of 550 HV0.3 at a distance from the surface of 0.15-0.30 mm (which can be particularly advantageous for concrete screws) or 0.1-0.15 mm (which can be particularly advantageous for self-tapping screws). This, in turn, can provide good resistance to thread wear, even when furrowing in

concrete and rebars, which in turn allows for a high bearing capacity of the screw. In addition, the dissolved nitrogen can increase the PRE index in the boundary zone locally to 23 or higher and thereby significantly improve the resistance to pitting corrosion, preferably to a level comparable to a 1.4401 steel. In particular, the electrochemical parameter of the “breakthrough potential” can be brought to a level comparable to a 1.4401 steel. The reason for the upper limit of the nitrogen partial pressure of 0.3 bar or 0.20 bar is that the formation of chromium-containing and/or nitrogen-containing precipitates can thereby be efficiently counteracted, which is advantageous in terms of corrosion resistance. The reason for the lower limit of the nitrogen partial pressure of 0.05 bar or 0.10 bar is that a significant effect of the nitrogen occurs only after reaching this pressure. The atmosphere provided in the step of case-hardening may be pure nitrogen or a gas mixture which has equivalent nitrogen activity at the given temperatures. In particular, a pure nitrogen atmosphere may be provided, provided that the process is carried out in a low-pressure furnace. In an atmospheric pressure furnace, dilution could be carried out with noble gases, for example.

[0028] Expediently, it may be provided that the case-hardening of the blank with nitrogen from the gas phase occurs in combination with a carburizing of the blank with carbon from the gas phase. Thus, in addition to an increase in the nitrogen content, it is additionally possible to provide an increase in the carbon content as a result of carbon being diffused from the gas phase. This embodiment is based on the recognition that, with simultaneous availability of carbon and nitrogen, the solubility of both elements can be increased simultaneously, wherein, with a higher nitrogen content and simultaneous avoidance of carbides and nitrides, a further advantageous increase in hardness and corrosion resistance can be achieved. In order to perform case-hardening of the blank with nitrogen from the gas phase in combination with carburizing the blank with carbon from the gas phase, gaseous nitrogenous and carbonaceous media, for example, may be introduced into the process chamber separately and alternately. Alternatively, a gas mixture that provides both carbon and nitrogen can be used (for example, ethyne, C₂H₂, along with N₂).

[0029] In particular, the method may comprise the step of “processing the blank”. In this step, the blank can be made into the shape of the shaped body. The processing may include, for example, forming a thread on the blank. In particular, the processing of the blank may include a non-cutting forming, in particular a cold-forming, preferably a rolling, of the blank. It is particularly preferred that the step of case-hardening of the blank takes place subsequent to the step of processing the blank. Accordingly, the blank is processed before hardening. The timing of the case-hardening subsequent to the processing can simplify the processing and ensure particularly homogeneous product properties.

[0030] The step of case-hardening may expediently be followed by a step of deep-freezing the blank, preferably at temperatures below minus 80° C., particularly preferably at a temperature of minus 150° C., and then annealing the blank, preferably at temperatures between 150° C. and 500° C., particularly preferably at temperatures between 200° C. and 250° C., and/or for hold times between 1 hour and 5 hours. As a result, an even higher hardness and/or toughness can be set without reducing the corrosion resistance.

[0031] The blank is expediently in the form of wire at the beginning of the process, i.e. it is a wire-shaped semi-finished product, which can further reduce the effort.

[0032] As already mentioned several times, the invention is particularly suitable for the production of screws. It is therefore particularly preferred that the shaped body is a screw shape, preferably with a screw shaft and a thread arranged on the screw shaft. The screw shape can form part of a finished screw or preferably the entire screw at the end of the method, which is to say that preferably a monolithic screw is provided.

[0033] In particular, a local induction hardening of a tip region of the screw shape and, preferably, thereafter a deep-freezing of the screw shape can be provided. Inductive hardening at the screw tip can provide a localized increase in hardness to 580-700 HV0.3 without compromising toughness in failure-critical areas of the screw, such as in the head, underhead and/or shaft area.

[0034] The invention also relates to the aforementioned steel as such, namely a steel with 0.07 to 0.14% carbon by weight, preferably 0.08 to 0.12% carbon by weight, 13 to 15% chromium by weight, 1.3 to 1.7% molybdenum by weight, 1.5 to 2.0% nickel by weight and 1.0 to 1.5%, preferably 1.2% manganese by weight.

[0035] The invention also relates to the use of a steel according to the invention for producing a screw and/or a screw which at least partially comprises a steel according to the invention and/or which is obtainable, and in particular is obtained, in a method according to the invention. The screw may preferably be a self-tapping screw. It can for example be a concrete screw, that is a screw for cutting into concrete, or a self-tapping screw for metal sheets. Preferably, the screw is a monolithic screw.

[0036] The ratio of the outer diameter of a thread of the screw to the thread pitch of the thread may be in the range of 1 to 2, in particular in the range of 1.2 to 1.45. These are typical thread dimensions for screws intended for self-tapping screwing into mineral substrates such as concrete. Thread pitch is understood in particular to mean the axial distance of successive turns of a thread. According to the invention, a concrete substrate may be provided with a bore into which a screw according to the invention is screwed, wherein in the concrete substrate, a negative form of the cutting thread of the screw is formed. Accordingly, the screw is screwed into the bore in the concrete substrate in a self-tapping manner to form a counter-thread.

[0037] Preferably, the steel according to the invention contains 0.08 to 0.12 wt % carbon, whereby even more advantageous material properties can be achieved, especially with regard to screw applications.

[0038] Features are used which are explained in connection with the method according to the invention, the steel according to the invention, the use according to the invention, or the screw according to the invention, are not intended to be limited to this category but can also be applied to the other category, that is to say method, steel, use or screw.

[0039] The invention is explained in more detail below with reference to preferred exemplary embodiments, which are shown schematically in the accompanying figures, wherein individual features of the exemplary embodiments shown below can be basically realized individually or in any desired combination in the context of the invention. The figures show schematic illustrations, in which:

[0040] FIG. 1 shows a schematic flow diagram of a production method according to the invention; and

[0041] FIG. 2 shows a schematic representation of a screw according to the invention, produced in a production method according to the invention.

[0042] FIG. 1 schematically shows the sequence of steps of a possible embodiment of a production method according to the invention. First, in step 1, a blank, preferably wire-shaped, made of a steel containing 0.07 to 0.14% carbon by weight, preferably 0.08 to 0.12 wt % carbon, 13 to 15 wt % chromium, 1.3 to 1.7 wt % molybdenum, 1.5 to 2.0 wt % nickel, and 1.0 to 1.5 wt % manganese. In addition, the steel may have other admixtures customary in steel, for example vanadium (in particular <0.2% by weight), niobium (in particular <0.2% by weight), titanium (in particular <0.2% by weight) and/or silicon (in particular <0.5% by weight). The remainder is iron with unavoidable impurities, for example sulfur and/or phosphorus, in particular <0.02% by weight in each case.

[0043] Then, the blank is processed in step 2, for example, formed, preferably rolled, and the blank thereby made into the shape of a shaped body, in particular in the form of a screw shape with a screw shaft 20 and a thread 21 arranged on the screw shaft 20. Optionally, the screw shape may also have a rotary drive 15, for example a screw head, arranged on the screw shaft 20. In this case, step 2 of the processing may include, in addition to rolling, compression of the blank.

[0044] The blank formed as a screw shape is then hardened in step 3 at a temperature greater than 900° C., especially between 1,000° C. and 1,150° C., more preferably between 1,030° C. and 1,100° C., in a nitrogenous gas atmosphere, wherein the nitrogen partial pressure of the gas atmosphere is preferably between 0.05 bar and 0.6 bar, more preferably less than 0.3 bar and particularly preferably less than 0.20 bar. Optionally, the gas atmosphere may also contain carbon.

[0045] Subsequently, the blank formed as a screw shape is quenched in step 4, in particular gas-quenched.

[0046] In the subsequent step 5, a deep-freeze treatment of the form of a screw blank follows at temperatures below minus 80°, for example at minus 150° C.

[0047] Finally, the blank formed as a screw shape is annealed in step 6, preferably in a temperature range between 150° C. and 500° C., more preferably between 200° C. and 250° C., and/or for a holding time between 1 hour and 5 hours.

[0048] Optionally, in a subsequent step 7, a local, preferably inductive, hardening can be provided at a tip region of the blank designed as a screw shape, and preferably a subsequent deep-freezing of the blank formed as a screw shape can be provided.

[0049] An exemplary embodiment of a screw according to the invention, which is formed as a concrete screw, is shown in FIG. 2.

[0050] The screw 10 has a cylindrical screw shaft 20, at the end of which a hexagonal screw head is provided which forms a rotary drive 15. Along the screw shaft 20, a thread 21 formed as a cutting thread extends with an outer diameter *d* and a pitch *p*. Optionally, a smaller-diameter support thread 28 may be provided on the screw shaft 20.

[0051] The screw shaft 20 of the screw is screwed into a bore in a mineral substrate 50, in particular in a concrete substrate, wherein the thread 21 formed as a cutting thread

has cut open a corresponding thread in the substrate 50 during screwing. The screw shaft 20 is guided through a hole in an attachment 53 which is secured to the substrate 50 by the rotary drive 15 formed as a screw head.

1. A method for producing a shaped body, the method comprising producing a blank comprising a steel with 0.07 to 0.14 wt % carbon, 13 to 15 wt % chromium, 1.3 to 1.7 wt % molybdenum, 1.5 to 2.0 wt % nickel and 1.0 to 1.5 wt % manganese.

2. The method according to claim 1, including case-hardening the blank with nitrogen from the gas phase.

3. The method according to claim 2, including the case-hardening the blank with nitrogen from the gas phase in combination with carburizing the blank with carbon from the gas phase.

4. The method according to claim 2, including processing the blank, wherein case-hardening the blank is performed subsequent to processing the blank.

5. The method according to claim 1, including deep-freezing the blank at temperatures below minus 80° C. and subsequently annealing the blank at temperatures between 150° C. and 500° C.

6. The method according to claim 1, wherein the shaped body is a screw shape.

7. The method according to claim 6, including local induction hardening of a tip portion of the screw shape.

8. A steel comprising 0.07 to 0.14 wt % carbon, 13 to 15 wt % chromium, 1.3 to 1.7 wt % molybdenum, 1.5 to 2.0 wt % nickel and 1.0 to 1.5 wt % manganese.

9. A screw produced using the steel of claim 8.

10. A screw at least partially comprising a steel obtainable in the method according to claim 1.

11. A screw according to claim 10, having a ratio of an outside diameter (*d*) of a thread of the screw to a thread pitch (*p*) of the thread is in the range of 1 to 2.

12. The method according to claim 2, comprising case-hardening the blank with nitrogen from the gas phase at temperatures between 1,000° C. and 1,150° C.

13. The method according to claim 2, comprising case-hardening the blank with nitrogen from the gas phase at a nitrogen partial pressure between 0.05 and 0.3 bar.

14. The method according to claim 12, comprising case-hardening the blank with nitrogen from the gas phase at a nitrogen partial pressure between 0.05 and 0.3 bar.

15. The method according to claim 3, including processing the blank, wherein case-hardening the blank is performed subsequent to processing the blank.

16. The method according claim 2, including deep-freezing the blank at temperatures below minus 80° C. and subsequently annealing the blank at temperatures between 150° C. and 500°.

17. The method according claim 3, including deep-freezing the blank at temperatures below minus 80° C. and subsequently annealing the blank at temperatures between 150° C. and 500°.

18. The method according claim 4, including deep-freezing the blank at temperatures below minus 80° C. and subsequently annealing the blank at temperatures between 150° C. and 500°.

19. The method according to claim 2, wherein the shaped body is a screw shape.

20. The screw according to claim **11**, wherein the ratio of the outside diameter of the thread to the thread pitch is in the range of 1.2 to 1.45.

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