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(54) METHOD FOR SURFACE HARDENING A COLD DEFORMED ARTICLE COMPRISING LOW TEMPERATURE ANNEALING

(57) The present invention relates to a method for surface hardening a cold deformed article at least partially consisting of stainless steel or a nickel base alloy with a chromium content of at least 10 % by weight, comprising the steps of:

a) providing a cold deformed article, wherein at least the surface region of the article is made of an alloy selected from the group consisting of stainless steel and nickel base alloys with a chromium content of at least 10 % by weight,

b) annealing the cold deformed article for 1 minute to 100 hours at a temperature between 300°C and 900°C in a non-carburizing atmosphere, a non-nitriding atmosphere and a non-nitrocarburizing atmosphere (i.e. atmosphere containing no compound nitrogen containing compound and no carbon containing compound),

c) activating the annealed article obtained in step b) and d) simultaneously with step c) or after step c) heat treating the annealed article at a temperature of 100 to less than 550°C in plasma, in a salt bath or in a gaseous atmosphere to obtain a nitride, carburized and/or nitrocarburized diffusion zone in the surface area of the article, wherein the plasma, the salt bath or the gaseous atmosphere contains a compound selected from the group consisting of carbon, nitrogen containing compounds, carbon containing compounds and mixtures of two or more of the aforementioned compounds,

wherein the annealing in step b) is performed with a higher temperature than the heat treating in step d). In addition, the present invention relates to a surface hardened cold deformed article obtainable with this method.

EP 3 299 487 A1

Description

[0001] The present invention relates to a method for surface hardening a cold deformed article at least partially consisting of stainless steel or a nickel base alloy with a chromium content of at least 10 % by weight. Moreover, the present invention relates to a surface hardened cold deformed article obtainable with this method.

[0002] Articles, such as metal articles made of steel or a nickel base alloy, are often shaped by means of cold deformation, such as extrusion or cold forging. Cold deformation is a method for strengthening a metal by plastic deformation, which is usually performed in the course of shaping an article at a temperature below the recrystallization temperature of the material, from which the article is made. Stainless steels, such as austenitic stainless steel, usually have an excellent corrosion resistance, toughness and weldability, but have a comparable low yield strength as well as a comparable low wear resistance. Cold forming improves the yield strength of such articles on account of structural changes, i.e. in particular changes of the microstructure, such as the formation of martensite and the like, in the steel occurring as consequence of the plastic deformation occurring during the cold working.

[0003] In particular for improving the wear resistance and for increasing specifically the surface hardness of articles made of stainless steel and comparable alloys, such articles are often also diffusion hardened in addition to the cold working, by subjecting the articles to a heat treatment at a temperature of typically 350 to 510°C in an atmosphere comprising a chemical compound forming during the heat treatment a species, which diffuses into the surface of the articles and thus improves the characteristics of the articles. Most prominent diffusion hardening methods are carburizing, nitriding and nitrocarburizing. While carbon diffuses during carburization into the surface area of the article, nitrogen diffuses during nitriding, carbon and nitrogen diffuse during nitrocarburizing and boron diffuses during boriding into the surface area of the article. Carburization, for example, is performed by heat treating the article in an atmosphere containing for instance an alkane, such as propane, and optionally further including hydrogen at 500°C for 10 hours. The article has to be activated during or better before the carburization, in order to remove the oxide layer of the article, which would act during the carburization as barrier. Such an activation is usually performed in a fluorine compound containing atmosphere, such as in a gaseous atmosphere comprising NF_3 at a temperature of 250 to 500°C, such as for instance described in EP 0 678 589 A1.

[0004] A major disadvantage of diffusion hardening cold worked articles made of stainless steel or comparable alloys is that as consequence of the microstructural changes of the stainless steel or alloy, respectively, occurred during the cold working, compounds consisting of the diffusion element and of chromium from the stainless steel or alloy, respectively, precipitate during the diffusion hardening. For instance, chromium carbide precipitates in the surface area of a cold worked stainless steel article during the carburization, chromium nitride precipitates in the surface area of a cold worked stainless steel article during the nitridation and chromium carbide as well as chromium nitride precipitate in the surface area of a cold worked stainless steel article during the nitrocarburization. On account of this, however, the free chromium content is reduced in the surface area of the cold worked and diffusion hardened stainless steel article, which significantly reduces its corrosion resistance.

[0005] In order to overcome these disadvantages, it has been already proposed to use for such cases specific stainless steel alloys, which are less prone to the formation of chromium rich precipitates. However, these specific stainless steel alloys are quite expensive so that they can be used only for expensive special products. Apart from that, for certain applications only materials are admitted, which are not less prone to the formation of chromium rich precipitates. The admission of the specific stainless steel alloys for specific applications would last at least 5 to 10 years. Apart from that, these specific stainless steel alloys are not readily available.

[0006] Furthermore, it was suggested to reduce the time and temperature of the diffusion hardening in order to limit the amount of chromium rich precipitate formed during the diffusion hardening process. However, this leads to only very thin diffusion hardened surface areas, which is for many applications inacceptable.

[0007] Thirdly, it has been proposed to perform a solution annealing process with the cold worked article before subjecting it to the diffusion hardening process at a comparable high temperature of above 1.000°C. However, this process leads to a significant reduction of the mechanical strength and hardness, namely of the surface hardness as well as of the hardness beneath the surface area of the article, which is inacceptable for most applications.

[0008] Finally, it has been suggested for this purpose for instance in WO 2013/0159781 A1 to conduct a solution nitriding treatment with the cold worked article before subjecting it to the diffusion hardening process. However, the effect of this method is comparable low. More specifically, even if maintaining the surface hardness, this process leads to a significant reduction of the hardness beneath the surface area of the article, which is inacceptable for most applications.

[0009] In view of all this, the object underlying the present invention is to provide a method for surface hardening a cold deformed article at least partially consisting of stainless steel or a nickel base alloy with a chromium content of at least 10 % by weight, which leads to an article with an excellent surface hardness, a high hardness beneath the surface area of the article, an excellent yield strength, a high wear resistance as well as an excellent corrosion resistance.

[0010] In accordance with the present invention this object is satisfied by providing a method for surface hardening a

cold deformed article at least partially consisting of stainless steel or a nickel base alloy with a chromium content of at least 10 % by weight, comprising the steps of:

a) providing a cold deformed article, wherein at least the surface region of the article is made of an alloy selected from the group consisting of stainless steel and nickel base alloys with a chromium content of at least 10 % by weight,
b) annealing the cold deformed article for 1 minute to 100 hours at a temperature between 300°C and 900°C in a non-carburizing atmosphere, a non-nitriding atmosphere and a non-nitrocarburizing atmosphere,
c) activating the annealed article obtained in step b) and
d) simultaneously with step c) or after step c) heat treating the annealed article at a temperature of 100 to less than 550°C in plasma, in a salt bath or in a gaseous atmosphere to obtain a nitride, carburized and/or nitrocarburized diffusion zone in the surface area of the article, wherein the plasma, the salt bath or the gaseous atmosphere contains a compound selected from the group consisting of carbon, nitrogen containing compounds, carbon containing compounds and mixtures of two or more of the aforementioned compounds,

wherein the annealing in step b) is performed with a higher temperature than the heat treating in step d).

[0011] This solution bases on the surprising finding that by performing an annealing step with the cold deformed article for 1 minute to 100 hours at a temperature between 100°C and 900°C, before subjecting the so treated article to an activation and low temperature diffusion hardening process, a precipitation of chromium rich agglomerates can be completely or at least to a great extent suppressed, even if the article has been cold formed. On account of this, the free chromium content of the alloy of the article and - as consequence thereof - also the corrosion resistance of the article in general and specifically of the surface area of the article is not reduced or, if at all, only insignificantly reduced. In contrast thereto, a respective method without performing the aforementioned annealing step would lead to the generation of significant amounts of chromium containing precipitates in the article leading to a significant reduction of the corrosion resistance of the article.

[0012] In view of this, the process in accordance with the present invention does not only lead to a high hardness of the article over its whole thickness as a consequence of the cold working as well as to an extremely high surface hardness as a consequence of the diffusion hardening, but in addition to an excellent wear resistance and corrosion resistance of the article on account of the annealing step. In advantage to articles having been merely cold formed, the articles obtained with the method in accordance with the present invention have a significantly increased surface hardness and an improved wear resistance. Furthermore, in advantage to articles having been cold formed and solution annealed, before having been subjected to a diffusion hardening, the articles obtained with the method in accordance with the present invention have an increased surface hardness, an improved hardness beneath the surface area of the article as well as an improved wear resistance. In addition, in advantage to articles having been cold formed and subjected to solution nitriding treatment, before having been subjected to a diffusion hardening, the articles obtained with the method in accordance with the present invention have an increased hardness beneath the surface area of the article as well as an improved wear resistance. Finally, in advantage to articles having been cold formed and subjected to an activation and a low temperature diffusion hardening without annealing heat treatment there between, the articles obtained with the method in accordance with the present invention have an increased corrosion resistance.

[0013] Cold forming in the sense of the present patent application, which is typically also called work hardening or strain hardening, is a method of strengthening a metal-article by plastic deformation. The strengthening occurs on account of dislocation movements and dislocation generation within the crystal structure of the material. Usually, cold forming is also used for shaping or forming the article, respectively, and is in general performed at a temperature below the full recrystallization temperature of the material, from which the article consists.

[0014] Generally, the annealing step b) of the method in accordance with the present invention may be performed at any temperature between 300°C and 900°C and for any time between 1 minute and 100 hours, as long as it is performed in a non-carburizing atmosphere, a non-nitriding atmosphere and a non-nitrocarburizing atmosphere, i.e. in an atmosphere which is non-carburizing atmosphere, non-nitriding and non-nitrocarburizing. Preferably, the non-carburizing, non-nitriding and non-nitrocarburizing atmosphere contains no compound selected from the group consisting of nitrogen containing compounds, carbon containing compounds and mixtures of two or more of the aforementioned compounds. Nitrogen and/or carbon may be included in the atmosphere of step b), as long as step b) is performed at a temperature, at which the nitrogen and/or carbon is not diffused into the surface of the substrate. So the annealing step b) may be performed in a pure nitrogen atmosphere at a temperature below 850°C, since then no nitriding occurs.

[0015] Of course, the temperature and duration of the annealing step b) slightly depends on the precise composition of the alloy, from which the article to be treated is made. Typically, the more severe the conditions during the annealing step, the more the hardness of the article decreases, but on the other hand the better the chromium containing precipitate generation is suppressed during the later diffusion hardening process. According to a preferred embodiment of the present patent application, the annealing step b) is conducted for a duration and at a temperature selected from the aforementioned numeric value ranges so that the hardness of the cold worked article is not reduced in average by more

than 15% during the annealing step b). In other words, the annealing step b) is preferably performed so that the hardness of the cold worked and annealed article is in average at least 85% of the hardness of the cold worked article before annealing. Hardness means in this connection the Vickers hardness.

[0016] Taking the above into account, the annealing step b) is preferably performed for a time of 1 minute to 100 hours, more preferably for 5 minutes to 50 hours, even more preferably for 10 minutes to 20 hours and most preferably for 20 minutes to 10 hours.

[0017] Good results are in particular obtained, if the annealing step b) of the method in accordance with the present invention is performed at a temperature between 350°C and 800°C, more preferably at a temperature between 450 and 750°C and most preferably at a temperature between 550 and 700°C.

[0018] Particular good results are obtained, when the annealing step b) of the method in accordance with the present invention is performed for 20 minutes to 10 hours at a temperature between 550°C and 700°C.

[0019] The present invention is not particularly limited concerning the pressure, at which the annealing step b) is conducted. For instance, the annealing step b) may be performed at atmospheric pressure or under reduced pressure. As set out above, the annealing step is performed in a non-carburizing atmosphere, a non-nitriding atmosphere and a non-nitrocarburizing atmosphere, i.e. in an atmosphere containing no compound selected from the group consisting of nitrogen containing compounds, carbon containing compounds and mixtures of two or more of the aforementioned compounds that would form diffusible compounds during the annealing step. Otherwise, a diffusion of carbon and/or nitrogen would occur during the annealing step b) at least to a small degree and this would initiate the formation of chromium containing precipitates, which would oppose the effects achieved with the method in accordance with the present invention. Moreover, it has been found during the present invention that the effects of the annealing step b), namely the reduction of chromium containing precipitates during the later diffusion hardening, are in a particular excellent extent obtained, when the annealing step b) is performed in an atmosphere which does not lead to a structural change of the surface, in particular to a change of the surface roughness and surface morphology of the article. In particular, it is of advantage that the oxide layer of the article is maintained during the annealing step b).

[0020] In view of this, it is preferred in accordance with a first preferred alternative of the present invention that the annealing step b) is performed under vacuum, namely preferably at a pressure of at most 10.000 Pa and more preferably of at most 5.000 Pa.

[0021] Alternatively, it is preferred in accordance with a second preferred alternative of the present invention that the annealing step b) is performed in an atmosphere, which also- i.e. in addition to diffusible compounds selected from the group consisting of nitrogen containing compounds, carbon containing compounds and mixtures thereof - does not include any compound, which would remove or even partially remove the oxide layer on the alloy, from which the article is made, during the annealing step b). Accordingly, it is preferred in this second alternative that the annealing step b) is performed in an atmosphere, which does not contain more than 5 % by volume of fluorine, of a fluorine containing compound and/or of a fluoride containing compound, preferably not more than 1 % by volume of fluorine, of a fluorine containing compound and/or of a fluoride containing compound, preferably not more than 0.1 % by volume of fluorine, of a fluorine containing compound and/or of a fluoride containing compound and most preferably no fluorine, no fluorine containing compound and no fluoride containing compound at all. On account of the same reasons it is preferred in this second alternative that the annealing step b) is performed in an atmosphere, which does not contain more than 5 % by volume of chlorine, of a chlorine containing compound and/or of a chloride containing compound, preferably not more than 1 % by volume of chlorine, of a chlorine containing compound and/or of a chloride containing compound, preferably not more than 0.1 % by volume of chlorine, of a chlorine containing compound and/or of a chloride containing compound and most preferably no chlorine, no chlorine containing compound and no chloride containing compound at all.

[0022] In a further development of the aforementioned second alternative, it is suggested that the annealing step b) is performed in a reducing atmosphere, which assures that the oxide layer of the article is maintained during the annealing step b). Good results are in particular obtained, when the annealing step b) is performed in an atmosphere containing hydrogen.

[0023] As set out above, at least the surface region of the article is made of an alloy selected from the group consisting of stainless steel and nickel base alloys with a chromium content of at least 10 % by weight. However, it is preferred that the whole article consists completely of the alloy.

[0024] Good results are for example obtained, when the cold deformed article provided in step a) consists of austenitic stainless steel and/or duplex stainless steel.

[0025] In accordance with the present invention there is no limitation concerning the thickness of the article and surprisingly good results are even obtained with comparable thick articles, which may be not processed for example with a method of the prior art comprising a solution nitriding treatment of the cold worked article before subjecting it to the diffusion hardening process. In particular, the method in accordance with the present invention is suitable for articles having a thickness of at least 100 μm and even for articles having a thickness of at least 5 mm.

[0026] The cold forming for obtaining the article provided in step a) may be any cold forming step known to a person skilled in the art. Exemplarily, the step a) may comprise plastically deforming the article at a temperature of at most

300°C, preferably by a technique selected from the group consisting of forging, extrusion, shaping, drawing, pressing, roll burnishing, rolling and combinations of two or more of the aforementioned techniques.

[0027] Alternatively thereto, step a) may comprise the machining of the article at a temperature of at most 200°C, preferably by a technique selected from the group consisting of turning, milling, punching, grinding, polishing and combinations of two or more of the aforementioned techniques.

[0028] It is also possible that the two aforementioned cold forming techniques are combined, namely that step a) comprises plastically deforming the article at a temperature of at most 300°C and machining the article at a temperature of at most 200°C, wherein the plastically deforming is preferably performed by a technique selected from the group consisting of forging, extrusion, shaping, drawing, pressing, roll burnishing, rolling and combinations of two or more of the aforementioned techniques and wherein the machining preferably performed by a technique selected from the group consisting of turning, milling, punching, grinding, polishing and combinations of two or more of the aforementioned techniques.

[0029] In accordance with a preferred embodiment of the present invention, the heat treatment in step d) is performed as carburizing step in a gaseous atmosphere comprising a carbon containing compound. Good results are in particular obtained, when the carbon containing compound is selected form the group consisting carbon monoxide, carbon dioxide, mixtures of carbon monoxide and carbon dioxide, hydrocarbon compounds and mixtures of two or more of the aforementioned compounds, wherein the hydrocarbon compound is preferably selected from the group consisting of C_{1-6}-alkanes, fluorinated C_{1-6}-alkanes, C_{1-6}-alkenes, fluorinated C_{1-6}-alkenes, C_{1-6}-alkynes, fluorinated C_{1-6}-alkynes and mixtures of two or more of the aforementioned compounds, wherein C_{1-6}-alkynes and/or fluorinated C_{1-6}-alkynes are particularly preferred.

[0030] Optionally, the aforementioned carburization gas may further comprise hydrogen, which promotes the decomposition of the carbon containing compound and thus the formation of diffusible carbon.

[0031] Independently, from whether the carburization gas contains the optional hydrogen or not, the carburization gas may contain an inert gas, such as argon, as diluent.

[0032] In accordance with an alternatively preferred embodiment of the present invention, the heat treatment in step d) is performed as nitriding step in a gaseous atmosphere comprising a nitrogen containing compound. Good results are in particular obtained, when the nitrogen containing compound is ammonia and/or urea. Optionally, the aforementioned nitriding gas may further comprise hydrogen, in order to promote the decomposition of the nitrogen containing compound and thus the formation of diffusible nitrogen, and/or an inert gas, such as argon, as diluent.

[0033] In accordance with yet an alternatively preferred embodiment of the present invention, the heat treatment in step d) is performed as nitrocarburization step in a gaseous atmosphere comprising a carbon containing compound as well as a nitrogen containing compound. Good results are in particular obtained, when the nitrocarburization is performed in a gaseous atmosphere comprising i) carbon monoxide, carbon dioxide, a mixture of carbon monoxide and carbon dioxide and/or a hydrocarbon compound, wherein the hydrocarbon compound is preferably selected from the group consisting of C_{1-6}-alkanes, fluorinated C_{1-6}-alkanes, C_{1-6}-alkenes, fluorinated C_{1-6}-alkenes, C_{1-6}-alkynes, fluorinated C_{1-6}-alkynes and mixtures of two or more of the aforementioned compounds, and ii) a nitrogen containing compound, wherein the nitrogen containing compound is ammonia and/or urea. Optionally, the aforementioned nitrocarburization gas may further comprise hydrogen, in order to promote the decomposition of the carbon containing compound and of the nitrogen containing compound and thus the formation of diffusible nitrogen and carbon, and/or an inert gas, such as argon, as diluent.

[0034] In accordance with the present invention, the diffusion hardening performed during the heat treatment in step d) is performed as so called low temperature diffusion hardening at a temperature between 100 and less than 550°C in plasma, in a salt bath or in a gaseous atmosphere to obtain a nitride, carburized and/or nitrocarburized diffusion zone in the surface area of the article. Particular good results are obtained, when the diffusion hardening is conducted at a temperature between 350 and 510°C.

[0035] Preferably, the diffusion hardening is performed for 10 minutes to 100 hours, more preferably for 1 to 100 hours, even more preferably for 2 to 50 hours and most preferably for 5 to 20 hours.

[0036] The heat treatment in step d) is preferably performed at atmospheric or subatmospheric pressure between 500 and 10,000 MPa.

[0037] In accordance with a further preferred embodiment of the present invention, the heat treatment of the article in step d) is performed in plasma. Preferably, the plasma heat treatment step d) is performed in plasma at a pressure of 100 to 1.000 Pa for 10 minutes to 100 hours in a carburizing atmosphere, in a nitriding atmosphere or in a nitrocarburizing atmosphere at a temperature of 100 to 550°C.

[0038] If a carburizing atmosphere is used, the atmosphere preferably comprises carbon monoxide, carbon dioxide, a hydrocarbon compound, such as in particular methane, or a mixture thereof. If a nitriding atmosphere is used, the preferably oxygen free atmosphere preferably comprises ammonia and/or urea. If a nitrocarburizing atmosphere is used, the preferably oxygen free atmosphere preferably comprises i) carbon monoxide, carbon dioxide, a hydrocarbon compound, such as in particular methane, or a mixture thereof and ii) ammonia and/or urea. Independently, from whether

a carburizing atmosphere, a nitriding atmosphere or a nitrocarburizing atmosphere is used, the atmosphere may further contain an inert gas, such as argon, as diluent and/or hydrogen, in order to promote the decomposition of the carbon and/or nitrogen containing compound and thus the formation of diffusible carbon and/or nitrogen.

[0039] Particular good results are obtained, when the plasma heat treatment step d) is performed in plasma at a pressure of 100 to 1.000 Pa for 1 minute to 40 hours in a carburizing atmosphere, in a nitriding atmosphere or in a nitrocarburizing atmosphere at a temperature of 400 to 500°C.

[0040] During the plasma treatment not only a diffusion hardening is performed, but also an activation of the surface of the article, i.e. the removal of the oxide layer of the article, is achieved. In other words, the plasma treatment simultaneously fulfils the activation step c) and the diffusion hardening step d). However, in order to improve the activation efficiency, the activation in step c) is preferably performed before the heat treatment step d) and by sputtering the annealed article obtained in step b) preferably in an atmosphere comprising argon, hydrogen, a rare gas, such as helium, or a mixture thereof. The sputter activation step may be performed at a temperature between 100 and 550°C and preferably at a temperature of 300 to 500°C for 10 minutes to 10 hours and preferably for 1 to 10 hours.

[0041] In accordance with a further preferred embodiment of the present invention, the heat treatment of the article in step d) is performed in a salt bath. Preferably, the heat treatment is performed for 1 to 100 hours in a molten salt bath including as carbon donor and nitrogen donor a cyanide salt, such as sodium cyanide and/or potassium cyanide. In addition to the cyanide salt, preferably potassium chloride and lithium chloride are included in the salt bath and more preferably also an activator compound selected from the group consisting of barium chloride, strontium chloride, magnesium chloride, calcium chloride and mixtures of two or more of the aforementioned salts.

[0042] Particular good results are obtained, when the salt bath heat treatment step d) is performed in a salt bath for 30 minutes to 60 hours at a temperature of 100 to 500°C, preferably of 300 to 450°C and more preferably of 350 to 410°C.

[0043] During the treatment in the salt bath containing cyanide salt(s) not only a diffusion hardening is performed, but also an activation of the surface of the article, i.e. the removal of the oxide layer of the article, is achieved. In other words, the salt bath treatment simultaneously fulfils the activation step c) and the diffusion hardening step d).

[0044] In accordance with a further preferred embodiment of the present invention, the heat treatment of the article in step d) is performed in a gaseous atmosphere. The preferred temperature conditions, pressure conditions and gas compositions for carburization, nitridation and nitrocarburization have been described above. In this embodiment, the activation in step c) is preferably performed before the heat treatment step d) in a gaseous atmosphere comprising a fluorine compound at a temperature of 250 to 500°C. Preferably, the fluorine compound is selected from the group consisting of fluorine, NF_3, BF_3, CF_4, HF, SF_6, C_2F_6, WF_6, CHF_3, SiF_4, C_{1-6}-fluorinated alkanes, C_{1-6}-fluorinated alkenes, C_{1-6}-fluorinated alkynes and mixtures of two or more of the aforementioned compounds. Good results are in particular achieved in this embodiment, when the activation is performed at a temperature of 250 to 550°C and preferably of 350 to 500°C for of 0.5 to 50 hours and preferably 1 to 15 hours in a gaseous atmosphere including NF_3 and/or N_2 at atmospheric pressure.

[0045] Alternatively to the aforementioned embodiment, it is also possible to perform the activation according to step c) simultaneously with the heat treatment of the article in a gaseous atmosphere according to step d) for instance by using specific carbon containing compounds which also function as carbon donor. Suitable carbon containing compounds therefor are unsaturated C_{1-6}-hydrocarbon compounds, such as C_{1-6}-alkenes and C_{1-6}-alkynes, such as acetylene. Particularly suitable for this purpose are halogenates hydrocarbon compounds and in particular unsaturated halogenates hydrocarbon compounds, such as fluorinated C_{1-6}alkenes and fluorinated C_{1-6}-alkynes.

[0046] In order to reliably avoid a generation of chromium containing precipitates in the finally treated article, it is in a further development of the idea of the present invention as most preferably suggested that the method in accordance with the present invention does not comprise any heating to a temperature above 900°C, preferably does not comprise any heating to a temperature above 800°C, more preferably does not comprise any heating to a temperature above 750°C and most preferably does not comprise any heating to a temperature above 700°C.

[0047] Due to the same reasons, it is particularly preferred that the method in accordance with the present invention consists of steps a) to d) and optionally a cooling step between steps b) and c) to a temperature between 0°C and 100°C and preferably to a temperature between 23°C and 60°C and/or a cooling step between steps c) and d) to a temperature between 0°C and 100°C and preferably to a temperature between 23°C and 60°C.

[0048] In addition, the present invention refers to a surface hardened article obtainable by a method in accordance with the aforementioned method.

[0049] As set out above, the surface hardened article obtainable by a method in accordance with the present invention is characterized in that it does not only have a high hardness over its whole thickness as a consequence of the cold working as well as an extremely high surface hardness as a consequence of the diffusion hardening, but in addition an excellent wear resistance and corrosion resistance of the article on account of the annealing step.

[0050] More specifically, the surface hardened article in accordance with the present invention may have in average a Vickers hardness HV1 measured in accordance with ASTM E92-16 of at least 150, preferably of at least 200, more preferably of at least 210 and most preferably of at least 220.

[0051] In addition, the surface hardened article in accordance with the present invention may have surface hardness HV0.05 measured in accordance with ASTM E92-16 of at least 500, preferably of at least 600, more preferably of at least 650 and most preferably of at least 675.

[0052] Furthermore, the surface hardened article in accordance with the present invention may have a corrosion resistance measured in accordance with DIN EN ISO 8442-1 of December 1997 of less than 15 pitting corrosion points per 20 cm^2 surface area, preferably of less than 5 pitting corrosion points per 20 cm^2 surface area and more preferably of less than 1 pitting corrosion points per 20 cm^2 surface area.

[0053] Subsequently, the present invention is described by reference to an example and a comparative example, which, however, do not limit the scope of the present invention.

Example

[0054] First of all, a set of key lock washers was prepared from austenitic stainless steel AISI 316 by cold working. More specifically, key lock washers 2, each of which comprising a first side 3 with radial teeth 4 and an opposite camside 5 with cams 6, were prepared by fine blanking of the inner and outer diameter of each key lock washer and subsequently embossing the first side with radial teeth and the camside with a cold working tool.

[0055] Afterwards, so produced key lock washers were subjected to an annealing step, in which the key lock washers were heated for 1 hour at 700°C in a vacuum furnace in a vacuum of about 500 Pa. The heating-up was performed in the furnace with a rate of 50°C per minute.

[0056] Subsequently, the furnace was purged with 100 liter argon gas, before the annealed key lock washers were activated and simultaneously carburized at 420°C for 20 hours in an atmosphere comprising 5%by volume of acetylene, 50%by volume of hydrogen and 45%by volume of nitrogen.

[0057] The so obtained surface hardened key lock washers showed the following propertied:

	Surface hardened washers of the example
Base material hardness 1)	222 ± 11 HV1
Surface hardness 2)	690 to 890 HV0.05
Diffusion zone depth 3)	11 to 14 μm
Evaluation of corrosion resistance 4)	No Corrosion products are visible on the surface in an optical microscope at 100x magnification.
Evaluation of corrosion resistance 5)	Surface free form corrosion products (cf. fig. 2).
1) Measured in accordance with ASTM E92-16 2) Measured in accordance with ASTM E92-16 3) Determined in in dependence on DIN EN ISO 1463, 2004 with a Kalling II etchant at 1000x magnification 4) Determined in accordance with the Test described in EN ISO 8442-1, version of December 1997 5) Determined after immersion of the key lock washers for 68 hours in 200ml 3% NaCl for 68 hours at ambient temperature	

Comparative Example

[0058] A set of key lock washers was prepared and surface hardened as described in the example except that no annealing step was performed between the cold working and the carburization.

[0059] The so obtained surface hardened key lock washers showed the following propertied:

	Surface hardened washers of the comparative example
Base material hardness 1)	235 ± 13 HV1
Surface hardness 2)	680 to 840 HV0.05
Diffusion zone depth 3)	12 to 14 μm
Evaluation of corrosion resistance 4)	Corrosion products are visible on the surface and pitting corrosion spots can be seen in an optical microscope at 100x magnification.

(continued)

	Surface hardened washers of the comparative example
Evaluation of corrosion resistance 5)	Corrosion products are visible on the surface on the camside and the cutting edge on the inner diameter and the outer diamete (cf. fig. 3).
1) to 5) As described for the example	

List of Reference Numbers

[0060]

1 Set of key lock washers
2 Key lock washer
3 First side of Key lock washer
4 Radial teeth of Key lock washer 4
5 Cam-side of Key lock washer
6 Cams of Key lock washer

Claims

1. A method for surface hardening a cold deformed article at least partially consisting of stainless steel or a nickel base alloy with a chromium content of at least 10 % by weight, comprising the steps of:

a) providing a cold deformed article, wherein at least the surface region of the article is made of an alloy selected from the group consisting of stainless steel and nickel base alloys with a chromium content of at least 10 % by weight,
b) annealing the cold deformed article for 1 minute to 100 hours at a temperature between 300°C and 900°C in a non-carburizing atmosphere, a non-nitriding atmosphere and a non-nitrocarburizing atmosphere containing,
c) activating the annealed article obtained in step b) and
d) simultaneously with step c) or after step c) heat treating the annealed article at a temperature of 100 to less than 550°C in plasma, in a salt bath or in a gaseous atmosphere to obtain a nitride, carburized and/or nitrocarburized diffusion zone in the surface area of the article, wherein the plasma, the salt bath or the gaseous atmosphere contains a compound selected from the group consisting of carbon, nitrogen containing compounds, carbon containing compounds and mixtures of two or more of the aforementioned compounds,

wherein the annealing in step b) is performed with a higher temperature than the heat treating in step d).

2. The method in accordance with claim 1,
characterized in that
the annealing in step b) is performed in an atmosphere containing no compound selected from the group consisting of nitrogen containing compounds, carbon containing compounds and mixtures of two or more of the aforementioned compounds and preferably also no nitrogen and carbon.

3. The method in accordance with claim 1 or 2,
characterized in that
the annealing in step b) is performed for 1 minute to 100 hours at a temperature between 300°C and 800°C, wherein the annealing in step b) is preferably performed for 10 minutes to 100 hours at a temperature between 350°C and 800°C, more preferably at a temperature between 450 and 750°C and even more preferably at a temperature between 550 and 700°C.

4. The method in accordance with any of the preceding claims,
characterized in that
the annealing in step b) is performed under vacuum with a pressure of at most 10.000 Pa and preferably of at most 5.000 Pa or the annealing in step b) is performed in a reducing atmosphere, preferably an atmosphere containing hydrogen and more preferably an atmosphere consisting of hydrogen, at atmospheric pressure.

5. The method in accordance with any of the preceding claims,
characterized in that
the article consists of the alloy, wherein preferably the cold deformed article provided in step a) consists of austenitic stainless steel and/or duplex stainless steel and preferably has a thickness of at least 100 μm and preferably of at least 5 mm.

6. The method in accordance with any of the preceding claims,
characterized in that
step a) comprises plastically deforming the article at a temperature of at most 300°C, preferably by a technique selected from the group consisting of forging, extrusion, shaping, drawing, pressing, roll burnishing, rolling and combinations of two or more of the aforementioned techniques, and/or
step a) comprises machining the article at a temperature of at most 200°C, preferably by a technique selected from the group consisting of turning, milling, punching, grinding, polishing and combinations of two or more of the aforementioned techniques,
and/or
step a) comprises plastically deforming the article at a temperature of at most 300°C and machining the article at a temperature of at most 200°C, wherein the plastically deforming is preferably performed by a technique selected from the group consisting of forging, extrusion, shaping, drawing, pressing, roll burnishing, rolling and combinations of two or more of the aforementioned techniques and wherein the machining preferably performed by a technique selected from the group consisting of turning, milling, punching, grinding, polishing and combinations of two or more of the aforementioned techniques.

7. The method in accordance with any of the preceding claims,
characterized in that
the heat treatment in step d) is performed as carburizing in a gaseous atmosphere comprising a compound selected form the group consisting carbon monoxide, carbon dioxide, mixtures of carbon monoxide and carbon dioxide, hydrocarbon compounds and mixtures of two or more of the aforementioned compounds, wherein the hydrocarbon compound is preferably selected from the group consisting of C_{1-6}-alkanes, fluorinated C_{1-6}-alkanes, C_{1-6}-alkenes, fluorinated C_{1-6}-alkenes, C_{1-6}-alkynes, fluorinated C_{1-6}-alkynes and mixtures of two or more of the aforementioned compounds, wherein the gaseous atmosphere preferably further comprises hydrogen.

8. The method in accordance with any of the preceding claims,
characterized in that
the heat treatment in step d) is performed as nitriding in a gaseous atmosphere comprising a nitrogen containing compound and optionally further comprising hydrogen, wherein the nitrogen containing compound is preferably ammonia and/or urea.

9. The method in accordance with any of the preceding claims,
characterized in that
the heat treatment in step d) is performed as nitrocarburization in a gaseous atmosphere comprising i) a compound selected from the group consisting of carbon monoxide, carbon dioxide, a mixture of carbon monoxide and carbon dioxide, hydrocarbon compounds and mixtures of two or more of the aforementioned compounds and ii) a nitrogen containing compound, wherein the hydrocarbon compound is preferably selected from the group consisting of C_{1-6}-alkanes, fluorinated C_{1-6}-alkanes, C_{1-6}-alkenes, fluorinated C_{1-6}-alkenes, C_{1-6}-alkynes, fluorinated C_{1-6}-alkynes and mixtures of two or more of the aforementioned compounds, and wherein the nitrogen containing compound is preferably ammonia and/or urea, wherein the gaseous atmosphere preferably further comprises hydrogen.

10. The method in accordance with any of the preceding claims,
characterized in that
the heat treatment in step d) is performed at a temperature between 350 and 510°C, wherein the heat treatment in step d) is preferably performed for 10 minutes to 100 hours, more preferably for 1 to 100 hours, even more preferably for 2 to 50 hours and most preferably for 5 to 20 hours.

11. The method in accordance with any of the preceding claims,
characterized in that
the heat treatment of the article in step d) is performed in a gaseous atmosphere and the activation in step c) is performed by heat treating the article in a gaseous atmosphere comprising a fluorine compound at a temperature of 250 to 500°C, wherein the fluorine compound is preferably selected from the group consisting of fluorine, NF_3,

BF_3, CF_4, HF, SF_6, C_2F_6, WF_6, CHF_3, SiF_4, C_{1-6}-fluorinated alkanes, C_{1-6}-fluorinated alkenes, C_{1-6}-fluorinated alkynes and mixtures of two or more of the aforementioned compounds.

12. The method in accordance with any of the preceding claims,
characterized in that
the method does not comprise any heating to a temperature above 900°C, preferably does not comprise any heating to a temperature above 800°C, more preferably does not comprise any heating to a temperature above 750°C and most preferably does not comprise any heating to a temperature above 700°C.

13. A surface hardened article obtainable by a method in accordance with any of the preceding claims.

14. The surface hardened article in accordance with claim 13,
characterized in that
it has a Vickers hardness HV1 measured in accordance with ASTM E92-16 of at least 150, preferably of at least 200, more preferably of at least 210 and most preferably of at least 220,
and/or
it has a surface hardness HV0.05 measured in accordance with ASTM E92-16 of at least 500, preferably of at least 600, more preferably of at least 650 and most preferably of at least 675.

15. The surface hardened article in accordance with claim 13 or 14,
characterized in that
it has a corrosion resistance measured in accordance with DIN EN ISO 8442-1 of December 1997 of less than 15 pitting corrosion points per 20 cm^2 surface area, preferably of less than 5 pitting corrosion points per 20 cm^2 surface area and more preferably of less than 1 pitting corrosion points per 20 cm^2 surface area.

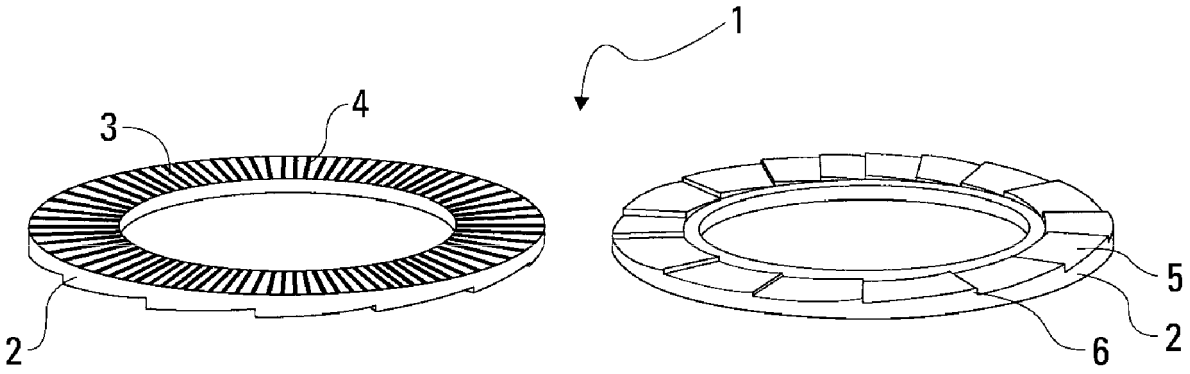

Fig. 1

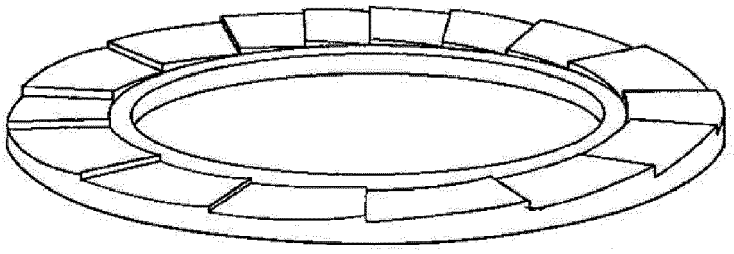

Fig. 2

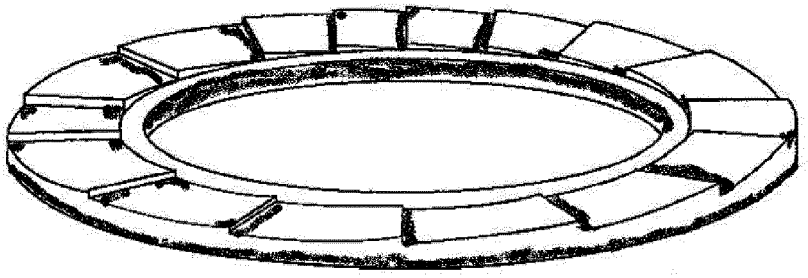

Fig. 3

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EUROPEAN SEARCH REPORT

Application Number
EP 16 19 0934

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Place of search	Date of completion of the search	Examiner
Munich	21 March 2017	Joffreau, P

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X : particularly relevant if taken alone
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