**Abstract:** A process for hardening steel workpieces and articles made therefrom, such as bearing rings, rolling elements, gears, cams, splines and lifters, comprising the steps of subjecting a workpiece steel to at least two sequential process segments wherein each process segment consists of subjecting the workpiece to a Boost period in an atmosphere containing active nitrogen, then subjecting the workpiece to a Diffuse period in an atmosphere free of active nitrogen to provide a desired target nitrided case depth in the steel workpiece in less time than in the prior art duplex hardening process with no deleterious intergranular network formation in the surface region.
Published: with international search report
DUPLEX HARDENING PROCESS AND ARTICLES MADE THEREFROM

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a new process for duplex hardening of steels and articles made by this process.

Description of Related Art

[0002] Duplex hardening of gears and bearing components is known in the art. The duplex hardening process is aptly named since it implies that the material is hardened by two methods. The material is first hardened by either carburization and quenching of a low carbon alloy steel grade (such as AMS 6278 steel) or by quenching a homogeneous high carbon alloy steel (such as AMS 6491 steel). Either material is further hardened by the addition of nitrogen to the surface. The purpose of this second hardening treatment is to increase the strength and hardness of the surface and near-surface region. The increased hardness of the material resists indentation by hard debris particles, which is particularly beneficial in bearings and gears.

[0003] The combination of the two hardening methods is relatively costly, so duplex hardening is used only for more highly alloyed, higher performance bearings and gears such as those used in aerospace applications. The earlier work involving duplex hardening showed no concern for the phenomenon of Inter Granular Network ("IGN") formation. More recently, there have been efforts to prevent formation of these networks by utilizing short process times and shallow hardening depth, as well as low nitriding potentials.

[0004] As nitrogen is added to the surface and diffuses into the near surface region, intragranular carbides dissolve and liberate their respective carbon atoms. The liberated carbon then diffuses further inward where it combines with iron at the grain boundaries to form cementite, Fe₃C (see Figure 1). This phenomenon is known by those skilled in the art as the "carbon push-ahead effect". It has been studied and found to occur in steels having carbon concentrations as low as 0.3% C. The IGN initially forms in the grain boundaries lying somewhat parallel to the surface. As the nitrogen concentration increases further, additional carbon arrives, and the IGN then forms in the grain boundaries not parallel to the surface.
U.S. Patent No. 6,966,954 to Rhoads et al. discloses a method for subjecting bearing material to a constant partial pressure of nitrogen. The steel workpieces are subjected to a lengthy, constant low nitriding potential atmosphere. This method is relatively easy to practice provided that precise control of gas flows is possible. It is important to keep the nitrogen concentration in the workpieces near the surface below 2.0% by weight because a deleterious IGN will form if the nitrogen concentration rises above approximately 2.0%. The workpiece is subjected to this constant atmosphere for up to 80 hours. The results of this process are not consistently acceptable because slight variations in furnace temperature and a variation in the amount of nitrogen input into the process can significantly influence the results of the process.

SUMMARY OF THE INVENTION

Briefly stated, the present invention is directed to a process for hardening steel workpieces and to articles made from those workpieces using that process such as bearing rings, rolling elements, gears, cams, splines and lifters, comprising the steps of subjecting a workpiece steel to at least two sequential process segments wherein each process segment consists of subjecting the workpiece to a Boost period in an atmosphere containing active nitrogen, then subjecting the workpiece to a Diffuse period in an atmosphere free of active nitrogen to provide a desired target nitrided case depth in the steel workpiece in approximately 30% less time than in the prior art duplex hardening process with no deleterious intergranular network formation at the case surface.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a photomicrograph showing the presence of cementite lying in grain boundaries after nitriding;

Fig. 2 is a graph comparing the nitrogen contents in the surface nitrided case of a conventionally processed workpiece and one processed according to the present invention;

Fig. 3 is a photomicrograph of a steel nitrided by a conventional process showing the presence of a deleterious IGN extending to the workpiece surface; and

Fig. 4 is a photomicrograph of a steel workpiece nitrided by the process of the present invention showing non-deleterious IGN spaced well below the surface of the workpiece.
DETAILED DESCRIPTION OF THE INVENTION

[0011] The present invention differs from the prior art process described above in that the workpiece is not subjected to a lengthy (up to 80 hours) constant, low active nitrogen (approximately 1%) source. The nitriding process of the present invention is of the Boost/Diffuse (BD) type. During a Boost period, the steel workpiece is subjected to a higher active nitrogen-containing atmosphere. A Diffuse period is conducted upon the termination of the Boost period. No additional nitrogen is added to the steel during the Diffuse period of the process. Due to gradients in chemical potential and concentration, the nitrogen existing inside the steel workpiece near the surface diffuses deeper into the steel during the Diffuse period. This diffusion of nitrogen away from the surface causes the concentration of nitrogen in the near-surface region to decrease. The rate of decrease is initially high and is proportional to the nitrogen concentration gradient existing in that region. As the nitrogen concentration decreases in the near-surface region of the steel workpiece, the nitrogen gradient decreases and the rate of nitrogen diffusion away from the surface decreases. A "process segment" according to the present invention consists of one Boost period and one Diffuse period.

[0012] A second process segment may follow the first process segment and begins with a second Boost period followed by a second Diffuse period. During the second Boost period of the second process segment, a source of active nitrogen is input into the process, additional nitrogen is deposited on the surface, and this nitrogen diffuses into the steel. The concentration of nitrogen in the near-surface region begins to increase after having declined during the aforementioned, first Diffuse period. After the second Boost period is concluded, a second Diffuse period is then conducted during which no active nitrogen is made available to the steel workpiece. After the second Diffuse period, the second process segment has been completed. The process cycle according to the present invention consists of two or more process segments comprising alternating periods of Boost and Diffuse. A consequence of at least two sequential process segments, each consisting of one Boost period and one Diffuse period, provides that a process segment always ends with a Diffuse period. This consequence allows for the nitrogen concentration in the near-surface region of the workpiece to be relatively lower than that provided in the constant low nitriding potential process of the prior art.
[0013] It will also be observed that the nitrogen concentration in the near surface region of
the workpiece during the Boost periods is periodically higher than that produced by the prior
art low constant nitriding potential process. This higher nitrogen concentration and higher
nitrogen gradient existing in the BD process of the present invention causes the development
of nitrided case to proceed faster. Thus, the target case depth of nitriding in the invention is
achieved in approximately 30% less time than the conventional process.

[0014] A possible consequence of nitriding steels is the formation of a compound layer at
the surface. In the process of the present invention, it is possible for thin sheets of the
compound layer to form at the surface in the relatively short time of the Boost period, but this
thin compound layer is easily dissolved into the steel as the nitrogen concentration in the near
surface region declines during the Diffuse period. During the lengthy conventional constant
nitriding potential process, there is no opportunity for any compound layer that forms to
dissolve; therefore, the known process is likely to produce more compound layer.

[0015] Nitrogen in the surface region can only diffuse deeper into the steel during the
Diffuse period. It cannot diffuse out of the steel because the process employs an atmosphere
that is not denitriding. When plasma nitriding is used in the Boost period of the present
process, the vessel is evacuated for the Diffuse period leaving no denitriding or decarburizing
species in the vessel. When gas nitriding is used in the Boost period, the vessel is then filled
with an inert gas such as argon for the Diffuse period which does not react with the steel
workpiece surface; thus, no denitriding is possible.

[0016] It is also necessary to prevent decarburization of the steel. Carbon diffuses out of
the steel under decarburizing conditions. Because there is no decarburizing agent present in
the BD process, it is unnecessary to add carbon to the steel during the Boost period of the BD
process of the present invention. The process employs an atmosphere that is neither
denitriding nor decarburizing—a vacuum in the case of plasma nitriding or an inert gas in the
case of gas nitriding.

[0017] Earlier, it was stated that the BD process of the present invention produces less IGN
in the steel workpiece than the prior art duplex hardening processes. In addition to this
benefit, the present process creates a unique nitrogen concentration profile. The
concentration profiles of the BD process of the invention and the known low constant
nitriding potential process of the prior art are depicted schematically in Figure 2. The
conventional process produces a nitrogen concentration curve that is mostly above that of the
BD process. A consequence of this phenomenon is that the conventional process will have a
greater probability of producing deleterious IGN close to the surface of the workpiece.

[0018] The situation is different for the present BD process. The relatively smaller volume
fractions of IGN produced in the BD process, if any, are to be found only near the deepest
penetrations of nitrogen. Because if IGN exists at all, it lies deep within the nitrided case and
it will not intersect the surface after grinding. The IGN will remain located well below the
surface of the steel workpiece. This is not the case for the constant low nitriding potential
process (see Figure 3). Intersections of IGN with the surface as shown in Figure 3 are
potential sites for the formation of cracks on a micro crack scale. Thus, the small amounts
of IGN that may be created within the present BD process that are spaced from the surface will
not contribute to spall formation. Figure 4 is an exemplary microstructure from a sample
prepared using the BD process. Comparison of Figures 3 and 4 shows the relative positions
of IGN in the two processes. Figure 4 clearly demonstrates the superiority of the present
process with respect to the non-existence of deleterious IGN at the surface of the steel
workpiece.

[0019] Several benefits of the BD duplex hardening process of the present invention may
be summarized as follows:

(a) Maintaining the nitrogen concentration low in the steel is easier because the
workpiece is not exposed to the source of nitrogen for the entire cycle time. Nitrogen is made
available to the steel surface for only relatively brief time periods. The present process is less
sensitive to variation about the mean in the input of nitrogen. The rate of decline of the
nitrogen concentration and the terminal value reached in the near-surface region during a
Diffuse period is self-correcting.

(b) Any IGN that may form in the steel during the present process consists of short
lengths situated deep within the nitried case. Thus, the small amounts of IGN, if present, do
not intersect the surface and are not deleterious to spall formation.

(c) The BD process cycle of the present invention is approximately 30% shorter than
the low constant nitriding potential duplex hardening process, thus providing obvious
economic benefits.

[0020] The steels that are candidates for this treatment for use in the workpieces such as
bearings or gears would have achieved prior to nitriding a minimum hardness of about 58
HRC extending from the surface to a depth based upon the component dimensions and
application. For some gears or bearings, the candidate steel would have achieved prior to nitriding a minimum hardness of about 60 HRC from the surface to a depth based upon the component dimensions and application. These levels of hardness can extend throughout the component depending upon the application requirements and the steel that is selected. This hardness can be achieved by either carburizing followed by quenching and tempering or by quenching and tempering alone. These alloys must also have sufficient tempering resistance during nitriding so that the hardness of the material meets application requirements at all depths after nitriding is completed. The tempering resistance is achieved by having the steel contain sufficient amounts of alloying elements such as Cr, Mo₃Si₅Ni, Co, Mn, and/or V or combinations thereof. The steels will also contain alloying elements that form nitrides such as Cr, Mo, V, Nb, and/or Al or combinations thereof. Examples of carburizing steels that are possible candidates include AMS 6278 (M50ni), CBS 223, AMS 5930 (Pyrowear 675), AMS 5932 (CSS42L), AMS 6749 (BG42), CBS 1000, and BS S132. Examples of steels that are candidates for quenching and tempering alone prior to nitriding are AMS 6491 (M50), M2, AMS 5630 (440C), ASTM T15, and AMS 5898 (Cronidur 30).

[0021] The workpieces being nitrided are steel components that otherwise are in a completed or nearly completed form. In one method, the steel used in these components will have been melted and worked into raw material forms such as billets, bars, rods or seamless tubes. Some applications would require the use of vacuum melting and refining techniques and may require multiple melting processes. Typical working methods would include one or more of the following processes: rolling, forging, piercing and ring rolling. The raw material would be cut into pieces that are directly machined or forged then machined into blanks corresponding to the rough geometry of the final components. Alternatively, the blank can be made by the consolidation of steel powders using such techniques as hot or cold isostatic pressing (HIP or CIP). The HIP or CIP may be preformed either directly to produce a blank or a preform such as a solid cylinder which is then worked and/or machined to blank dimensions. Blanks formed by any of these methods are heat treated either by a sequence of carburizing, quenching, and tempering or by a sequence of austenitizing in a non-carburizing atmosphere, quenching, and tempering. The quenching and tempering could either be performed by batch austenitizing and quenching or by surface hardening using techniques such as induction, laser or electron beam. Gaseous, pack, plasma or vacuum carburizing may be used. Quenching media may include air or other gas(es) or liquid(s). The quenchant may
be still or flowing or agitated. Carburized blanks may be rehardened for optimal properties. Multiple tempers may be performed on either carburized or direct quenched product. After this heat treatment sequence is completed, controlled amounts of material are removed from the blanks to dimensions that are near or at the final dimensions of the component. Material removal methods may include grinding, lapping, hardturning and/or honing. The nitriding process of the present invention is then carried out using gaseous, plasma, or salt bath techniques. Nitriding may be either the last manufacturing step carried out or can be followed by finishing processes using techniques such as grinding, lapping, hardturning, honing and/or superfinishing to achieve final dimensions and surface texture. Some areas of the workpiece may be prevented from nitriding due to fixturing or deliberate masking. Examples of the workpieces would be bearing rings, rolling elements and gears.

[0022] There are different nitriding process methods that may be compatible with the present BD process. Nitriding using a pulsed plasma hot-wall dc furnace has been successfully used by the inventors as described below. This type of furnace has an insulated external shell with heating elements so the workpiece temperature is maintained without relying on the heating produced by plasma generation. Therefore, the ion current during the Boost period can be selected as a variable independent of the workpiece temperature. Even more significantly, the workpiece temperature can be maintained during the Diffuse period when no plasma is being generated. It is anticipated that controlled gas nitriding is another means of performing the BD process. In this method, the nitrogen potential of the atmosphere within the furnace is determined automatically throughout the nitriding process. The measured nitrogen potential is compared to the setpoint value by the control system. The control system then adjusts the composition of the incoming gas mixture as needed to achieve the desired nitrogen potential. The required number of Boost/Diffuse process segments can be programmed into the controller for automatic operation.

[0023] Selection of the appropriate values for the key parameters for the nitriding process such as workpiece temperature, total nitriding time, percentage of time in Boost and active nitrogen potential during Boost depend upon the steel type, prior heat treatment, part geometry and material property requirements. The nitriding process parameters needed to produce the required properties in the workpiece are interdependent within ranges. The workpiece temperature is typically selected to minimize process time while preventing overtempering or softening. The workpiece temperature is expected to be in the range of
about 400°C to 600°C during nitriding. The time needed to absorb a given amount of nitrogen decreases rapidly as the workpiece temperature is increased. The total process time (Boost + Diffuse) is expected to be in the range of 40 to 80 hours. The Boost periods are expected to last about 2 to 20 hours while Diffuse periods may last from about 2 to 28 hours. The Boost periods may be of equal length or vary from one process segment to the next. Similarly, the Diffuse periods may be of equal length or vary from one process segment to the next. The percentage of total nitriding time spent in Boost periods is expected to range from 20 to 70% of the total process time. It is expected that the atmosphere would contain about 5 to 25 volume % active nitrogen during Boost periods. The amount of active nitrogen during each Boost period may be the same or could be varied.

[0024] Samples of quenched and tempered AMS 6491 steel and of carburized quenched and tempered AMS 6278 steel were pulse plasma nitrided using the BD process. The samples were ground after tempering and before nitriding. The total process time was about 20 to 60 hours. Up to 6 process segments were used. The preferred nitrogen concentration in the incoming gas mixture during the Boost periods was between about 10 to 20 volume %. The percentage of time spent in Boost was about 30 to 65% of the total process time. The nitriding temperature was between about 440°C and 524°C during both the Boost and Diffuse periods.

[0025] Within this range, a preferred condition for AMS 6491 and AMS 6278 steel was observed for a nitriding temperature of about 500°C and a total process time of about 60 hours with 6 process segments. The nitrogen concentration was between about 10 to 20 volume % in the incoming gas mixture during the Boost periods and the percentage of time in the Boost cycle was between about 30 to 50% of the total process time. The AMS 6491 samples prepared within this process range produced near surface hardness values equivalent to about at least 68 HRC compared to a pre-nitriding hardness of about 64 HRC while the AMS 6278 samples achieved near surface hardness values equivalent from about 65 HRC to at least 68 HRC compared to a pre-nitriding hardness of approximately 62 HRC. In the AMS 6491 samples, the depth to a hardness approximately equivalent to 67 HRC extended to depths of about 0.09 to 0.21 mm. The AMS 6278 samples exhibited a hardness approximately equivalent to 65 HRC to depths of about OJO to 0.20 mm. The concentration of IGN in samples of both materials observed using optical microscopy was much less than
that observed in Figure 3 and was typically located away from the surface as shown in Figure 4. In some samples, no IGN was observed at all using optical microscopy.

[0026] Additional samples of quenched and tempered AMS 6491 steel and of carburized quenched and tempered AMS 6278 steel were gas nitrided (as opposed to the above pulse plasma nitriding) using the present BD process. The samples were ground after tempering and before nitriding. The total process time was about 12 to 60 hours. Up to 6 process segments were used. The nitrogen potential, KN, in the incoming gas mixture during the Boost cycle was about 1 to 20. The percentage of time spent in the Boost periods was about 12 to 30% of the total process time. During the Diffuse cycle, the nitrogen potential was either reduced to less than about 1 or no nitriding potential was used. The temperature was about 500°C during both the Boost and Diffuse periods.

[0027] Within this range, a preferred condition for AMS 6491 and AMS 6278 steel was observed for a gas nitriding temperature of about 500°C and a total BD process time of about 60 hours with 6 process segments. The nitrogen potential, K_N, in the incoming gas mixture during Boost was between about 1.1 and 6, and the percentage of time in Boost was between about 20 to 30%. The AMS 6491 samples prepared within this process range produced near surface hardness values equivalent to about at least 68 HRC compared to a pre-nitriding hardness of about 62 HRC while the AMS 6278 samples achieved near surface hardness values equivalent from about 65 HRC to at least 68 HRC compared to a pre-nitriding hardness of approximately 62 HRC. In the AMS 6491 samples, the depth to a hardness approximately equivalent to 67 HRC extended to depths of about 0.08 to 0.21 mm. AMS 6278 samples exhibited a hardness approximately equivalent to 65 HRCD to depths of about 0.08 to 0.23 mm. The concentration of IGN in samples of both materials observed using optical microscopy was much less than that observed in Figure 3 and was typically located away from the surface as shown in Figure 4. In some samples, no IGN was observed at all using optical microscopy.

[0028] While specific embodiments of the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. The presently preferred embodiments described herein are meant to be illustrative only and not limiting as to the scope of the invention which is to be given the full breadth of the appended claims and any and all equivalents thereof.
THE INVENTION CLAIMED IS:

1. A process for nitriding a steel workpiece comprising the steps of:
   subjecting a workpiece steel to at least two sequential process segments
   wherein each process segment consists of subjecting the workpiece to a Boost period in an
   atmosphere containing active nitrogen, then subjecting the workpiece to a Diffuse period in
   an atmosphere free of active nitrogen.

2. The process of claim 1 wherein between two and six sequential process
   segments are used.

3. The process of claim 1 wherein the workpiece steel is a steel alloy
   selected from the group consisting of AMS 6491, AMS 6278 and similar steel alloys.

4. A bearing component made according to the process of claim 1.

5. A gear made according to the process of claim 1.

6. The process of claim 1 wherein the Boost period is conducted using
   one of gas or plasma nitriding.

7. The process of claim 1 wherein the treated workpiece has a near
   surface hardness of about 65 HRC or greater and having no intergranular network formation
   intersecting a surface of the workpiece.

8. The process of claim 1 carried out using one of controlled gas nitriding
   or pulse plasma dc hot wall nitriding during the Boost period.

9. The process of claim 1 wherein a total process time during all Boost
   and Diffuse periods is about 40 to 80 hours, comprising Boost periods of about 2 to 20 hours
   each, and Diffuse periods of about 2 to 28 hours each, wherein the Boost periods may be of
   equal length or vary from one process segment to the next, wherein the Diffuse periods may
   be of equal length or vary from one process segment to the next, wherein a percentage of total
   nitriding time spent in Boost periods is from about 20 to 70%, using active nitrogen contents
   of about 5 to 25 volume % during Boost periods, wherein an amount of active nitrogen used
during each Boost period may be the same or varied, and wherein a temperature is maintained between about 440 °C and 524 °C during both the Boost and Diffuse periods.

10. The process of claim 1 wherein a total of nitriding time during all Boost periods is about 60 hours, comprising Boost periods of about 3 to 5 hours each and Diffuse periods of about 5 to 7 hours, a percentage of total time spent in Boost periods is from about 20 to 50%, wherein active nitrogen contents of about 10 to 20 volume % are used during the Boost periods, and wherein a temperature of approximately 500 °C is maintained during both the Boost and Diffuse periods.

11. A process for nitriding one of a steel bearing component or a steel gear component comprising the steps of:

subjecting the steel component to at least two sequential process segments wherein each process segment consists of subjecting the steel component to a Boost period in an atmosphere containing active nitrogen, then subjecting the steel component to a Diffuse period in an atmosphere free of active nitrogen.

12. The process of claim 11 wherein the steel component is in one of a hardened or carburized and hardened condition prior to being subjected to the process segments.

13. The process of claim 11 wherein the steel component is one selected from the group consisting of AMS 6491 and AMS 6278 and the atmosphere containing nitrogen in an incoming gas during said Boost period has a nitrogen potential KN of between 1.1 and 6.

14. The process of claim 13 wherein a percentage of total time spent in Boost periods is between 20% to 30% of a total process time.
FIGURE 2
**INTERNATIONAL SEARCH REPORT**

**International application No**
PCT/US2007/080549

**A CLASSIFICATION OF SUBJECT MATTER**

| INV. | C23CB/26 | C21D1/76 | C21D9/32 | C21D9/40 |

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

**B FIELD SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
C21D C23C

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 practical, search terms used)
EPO-Internal, WPI Data

**C DOCUMENTS CONSIDERED TO BE RELEVANT**

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<td>X</td>
<td>WO 98/12361 A (TIMKEN CO [US]) 26 March 1998 (1998-03-26) page 10, line 26 - page 11, line 12; claims 1-16; figures 1,2</td>
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X Further documents are listed in the continuation of Box C X See patent family annex

* Special categories of cited documents

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