THREE STEP SURFACE ENHANCEMENT PROCESS FOR CARBON ALLOY FLUID ENDS

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ABSTRACT
A method for improving corrosion resistance and fatigue performance of a metallic surface of an article comprises nitrocarburizing the metallic surface to provide a nitrocarburized surface; forming an oxide layer on the nitrocarburized surface; and treating the oxide layer with a mechanical process.
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BACKGROUND

[0001] Hydraulic fracturing is a well stimulation technique generally undertaken utilizing high horse power trucks to pump high pressure fluids downhole to fracture rocks/shale. A well servicing truck consists of an engine, fan, transmission, power end, and fluid end. Typically, fluid ends will pump fluids at a pressure between about 3,000 psi to 15,000 psi. The fracturing fluids pumped with fluid ends carry particulates that are abrasive. The internal bores of a fluid end are subject to corrosion and erosion due to the presence of abrasives in the fluids, stresses, and localized cavitation. Erosion and corrosion causes pits, which can act as a stress riser or stress concentrator and provide an ideal location for the initiation of fatigue cracks. Accordingly, the fluid ends are susceptible to fatigue damage.

[0002] The industry has tried multiple solutions to address the erosion issue. One proposed solution is to build fluid ends from stainless steel instead of carbon steel. Compared to carbon steel, stainless steel has better corrosion resistance and fatigue properties. However, it is more expensive. In addition, it has been observed in the field that stainless steel fluid ends are susceptible to leaks in sealing areas. Thus, the industry is receptive to alternative approaches to improve the corrosion resistance and fatigue performance of carbon steel fluid ends.

SUMMARY

[0003] Disclosed is a method for improving corrosion resistance and fatigue performance of a metallic surface of an article. The method comprises: nitrocarburizing the metallic surface to provide a nitrocarburized surface; forming an oxide layer on the nitrocarburized surface; and treating the metallic surface with a mechanical deformation process after the oxide layer is formed.

[0004] An article comprising a treated metallic surface is also disclosed. The treated metallic surface comprises a diffusion layer and a compound layer from a nitrocarburization process, and an oxide layer from an oxidation process; wherein a compressive layer and a tensile layer from a mechanical deformation process are present in the treated metallic surface.

BRIEF DESCRIPTION OF THE DRAWINGS

[0005] The following descriptions should not be considered limiting in any way. With reference to the accompanying drawings, like elements are numbered alike:

[0006] FIGS. 1(a) and 1(b) show Optical Microscopy (OM) images of a surface treated with a nitrocarburization process;

[0007] FIG. 2 is a schematic illustration of a surface treated with a nitrocarburization process followed by oxidation;

[0008] FIG. 3 is an OM image of a surface treated with nitrocarburization followed by oxidation;

[0009] FIG. 4 illustrates stress profile of a mechanical surface treatment process such as shot peening, laser peening, and water jet peening;

[0010] FIGS. 5(a) and 5(b) show OM images of a carbon steel surface treated with nitrocarburization followed by shot peening;

[0011] FIG. 6 is a perspective view of a fluid end according to an embodiment of the disclosure.

[0012] FIG. 7 shows stress cycle curves of untreated carbon steel (sample A) in air; untreated carbon steel (sample A) in 15% HCl; shot peened carbon steel (sample B) in 15% HCl; carbon steel treated with ferritic nitrocarburization followed by oxidation in (sample C) 15% HCl; and carbon steel treated with ferritic nitrocarburization, oxidation, and shot peening (sample D) in 15% HCl respectively.

[0013] FIG. 8 is an optical microscopy image of a bare metal surface after a fatigue test in 15% HCl for about 9.25 hours.

[0014] FIG. 9 is an optical microscopy image of a mechanically treated metallic surface after a fatigue test in 15% HCl for about 18.25 hours.

[0015] FIG. 10 is an optical microscopy image of a thermochemically treated metallic surface after a fatigue test in 15% HCl for about 15.4 hours.

[0016] FIG. 11 is an optical microscopy image of a mechanically and thermochemically treated metallic surface after a fatigue test in 15% HCl for about 74 hours.

DETAILED DESCRIPTION

[0017] It is known that individual application of a thermochromical treatment or a mechanical treatment such as a mechanical deformation process can be beneficial for surface resistance, fatigue properties, and corrosion resistance. However, the beneficial effects of the individual treatment may not be sufficient for articles used in high pressure and highly corrosive environments.

[0018] Applicants have surprisingly found that a surface treated with a three-step process in the particular sequence of thermochemical treatment, oxidation, and mechanical deformation process significantly improves the corrosion resistance and fatigue life of the metallic surface, as compared to an untreated surface, a surface treated with the thermochemical process or a mechanical process alone, or a surface treated with the same three steps but in a different order.

[0019] The results are particularly surprising because one would expect that the impacts from a mechanical deformation process such as shot peening would damage a thermochemically treated surface. Further, if a surface is treated by a mechanical deformation process first followed by a thermochemical process, the benefit of the mechanical deformation process may be cancelled because the residual stress generated by the mechanical deformation process may be released during the thermochemical treatment.

[0020] The inventors have found that an introduction of an oxide layer between thermochemical and mechanical deformation treatments is surprisingly effective to preserve the effects of both the thermochemical and the mechanical treatment processes. The discovery allows the manufacture of corrosion resistant articles for a wide variety of applications. In particular, the three-step process can be used to treat the surface of a fluid end or components of a fluid end assembly thus improving the corrosion resistance and the fatigue life of the fluid end or fluid end assembly.

[0021] In an embodiment, a method for improving corrosion resistance and fatigue performance of a metallic surface of an article comprises nitrocarburizing the metallic surface to provide a nitrocarburized surface; forming an oxide layer on the nitrocarburized surface; and treating the metallic surface after the oxide layer is formed with a mechanical deformation process. The mechanical deformation process comprises shot peening, laser shock peening, water jet peening,
burnishing, cavitation peening, controlled impact peening, pinch peening, or a combination comprising at least one of the foregoing.

[0022] There are many types of diffusion based thermochemical surface treatment processes. An example of a thermal chemical surface treatment is shown in FIG. 1. These thermochemical treatments provide fatigue, corrosion, and wear resistance to the treated surface. The processes can vary based on the chemical, treatment temperature, and cooling rate. Nitrocarburization is a thermochemical surface treatment process. It diffuses both carbon and nitrogen into the metal surface, forming a solid solution and thereby entrapping diffused carbon and nitrogen atoms in the lattice of the metal. The layer containing the diffused carbon and nitrogen atoms is commonly referred to as a diffusion layer. Nitrocarburization can also produce a compound layer disposed on the diffusion layer. The compound layer contains Fe₃N, Fe₇N₃, or a combination comprising at least one of the foregoing. The depth of the compound and diffusion layers is process and material dependent. The compound layer can have a thickness of about 5 to about 25 microns, about 5 to about 20 microns, or about 5 to about 15 microns. The underlying diffusion layer can have a thickness of about 100 microns or more.

[0023] For surfaces comprising steels or other ferrous alloys, the nitrocarburization process is preferably a ferritic nitrocarburizing process carried out at a temperature of about 800 to about 1300°F, about 900 to about 1200°F, about 900 to about 1100°F, or about 1000°F to about 1100°F. In an embodiment, at least the surface of the article is heated in the presence of a gaseous medium or fluidized bed. The gaseous medium includes a nitrogen source and a carbon source.

Exemplary nitrogen source includes ammonia gas. Exemplary carbon source includes carbon dioxide, carbon monoxide, methanol, methane, ethane, propane, butane, pentane, or a combination comprising at least one of the foregoing. The carbon source can be an endothermic gas or exothermic gas. Nitrogen can be included in the gaseous medium. The nitrocarburization process may also be carried out by means other than a gaseous medium such as, for example, a salt spray bath or a plasma treatment or fluidized furnace. The process time ranges between about 30 minutes to about six hours or about one to about four hours.

[0024] Applicants have found that a nitrocarburization treated surface can have high porosity and can cause accelerated local corrosion. A secondary chemical/thermal process is used to address these disadvantages. The secondary process includes an oxidization process which generates an oxide layer on the compound layer. The oxide layer comprises Fe₃O₄ and can have a thickness of about 0.2 micron to about 2 microns or about 0.3 to about 1.5 microns. In an embodiment, the oxide layer is at least about 1 micron. A surface treated with nitrocarburization followed by oxidization is illustrated in FIG. 2. As shown in FIG. 2, the treated surface has an oxide layer 1, a compound layer 2, and a diffusion layer 3. An OM image of the treated surface is shown in FIG. 3.

[0025] The oxide layer can be formed by oxidizing the nitrocarburized surface at about 400°F to about 600°F for about 20 minutes to about 5 hours, or about 30 minutes to about 4 hours, or about one to about two hours. Other temperatures and duration of treatment are also contemplated. The nitrocarburization treated surface can be exposed to air, steam, or warm moist air during the oxidization process.

[0026] Either prior to the oxidization or after the oxidization, the nitrocarburized surface can be treated with wax sealant, powder sealant, or oil impregnation. The oxide layer improves lubricity, wear resistance, and fatigue properties of the material surface. The improvements are achieved by reducing the pore size of the compound layer as the oxide layer has smaller pore size than the compound layer. The retained wax or oil increases wear resistance.

[0027] A surface treated with nitrocarburization and oxidization can be further treated with a mechanical surface enhancement process to improve the corrosion resistance and the fatigue properties of the article. Exemplary mechanical surface enhancement processes include shot peening, laser shock peening, water jet peening, burning, such as low plasticity burnishing and roller burnishing, cavitation peening, controlled impact peening, pinch peening, or a combination comprising at least one of the foregoing. The mechanical surface enhancement processes are referred to as mechanical deformation processes.

[0028] Without wishing to be bound by theory, it is believed that these mechanical enhancement processes generate two types of stresses: a compressive stress on the treated surface and a tensile stress underneath the compressive stress. An exemplary residual stress profile of a surface treated with a mechanical surface enhancement process is illustrated in FIG. 4. As shown in FIG. 4, a mechanical enhancement process creates a compressive stress layer 4 and a tensile stress layer 5. The compressive stress layer acts as a protective layer from corrosion, crack initiation, and fretting fatigue. The tensile stress layer is present to balance the compressive stress in absence of an external force (equilibrium).

[0029] In an embodiment the mechanical enhancement process comprises shot peening. The shot materials include metallic materials, glass beads, ceramic materials, or a combination comprising at least one of the foregoing. Exemplary shot materials include S-440, S-550, S-660, or S-780. The average shot size can be about 0.04 inches or higher, about 0.055 inches or higher or about 0.04 inches to about 0.09 inches. The shot intensity can be about 0.014°F or higher, for example between about 0.014°F to about 0.016°F. The coverage of the shot peening treatment is about 100% to about 50%, about 100% to about 200%, about 100% to about 300%, or about 300%. Shot peening can be performed according to the procedure of SAE-AMS-2430.

[0030] As discussed above, the sequence of the three-step process is crucial for achieving the improved corrosion resistance and improved fatigue properties. For example, if a metal surface is treated with shot peening first followed by a nitrocarburization and an oxidization process, the corrosion resistance or fatigue properties may not be improved. Without wishing to be bound by theory, it is believed that the beneficial residual stresses generated from shot peening are not thermally stable. Exposure to thermal loading can relax residual stresses. It is further believed that at the operating temperatures of the nitrocarburization and the oxidization processes, the beneficial residual stresses created by shot peening may be released, thus the nitrocarburization and oxidization can cancel the benefits of shot peening.

[0031] Alternatively, if a mechanical surface treatment process, for example, shot peening, is used over a nitrocarburization treated surface, no beneficial effects on corrosion resistance or fatigue properties may be observed because the mechanical process can damage the compound layer formed from the nitrocarburization process. FIG. 5 is an OM image of carbon steel surface treated with a ferritic nitrocarburization
followed by shot peening. The figure shows that the protective compound layer has been damaged by impacts from shot peening.

[0032] The surface that can be treated with the three-step process comprises a metallic material. Exemplary metallic materials include plain carbon, medium carbon or low carbon alloy steel. In an embodiment, the surface comprises carbon steel. Carbon steel is used in reference to steel which is not stainless steel. As used herein, carbon steel may include alloy steels.

[0033] Various articles can be treated with the three-step process. Exemplary articles include pistons, plungers, pipes, steel balls, steel ball bearings, a fluid end, and a component of a fluid end assembly. In an embodiment, the article is a fluid end or a component of a fluid end assembly. An exemplary fluid end is shown in FIG. 6. As shown in FIG. 6, the fluid end has two bores: a vertical bore and a horizontal bore. The bottom end of the vertical bore is suction side (A) and the top end of the vertical bore is discharge side (B). Both the suction and discharge sides have pressure operated valves, namely, suction valve 6 and discharge valve 7. These valves open and close based on the pressure difference on the two sides of the valves. The left and right sides of the horizontal bore are plunger side (C) and suction cap side (D) respectively. The area between the valves, suction cover 9 and plunger 8 is called intersection bore (or pressure chamber) 10 and is subjected to cyclic high pressure and abrasive fluids. The plunger 8 is connected to the power end and creates pressure in the intersection bore.

[0034] The pressure in the intersection bore 10 is typically lower than suction pressure as the plunger is moving backward (out of the bore). The pressure difference opens the suction valve 6 and the intersection bore 10 is filled with fracturing fluid. The plunger starts to move backwards into the intersection bore after reaching the bottom dead center. Then the pressure in the intersection bore 10 starts to increase. The suction valve 6 closes when the pressure in the intersection bore 10 is higher than the suction pressure. The pressure in the intersection bore continues to increase as the plunger 8 moves forward. The discharge valve 7 opens when the pressure in the intersection bore 10 is higher than the discharge pressure. The discharge valve 7 closes when the pressure in the intersection bore 10 is lower than the discharge pressure. This entire process is repeated over and over again at high speeds (about 30 RPM to about 300 RPM). When the surface of the fluid ends or the components of the fluid ends, for example the intersection bore and the plunger, are treated with the three-step process disclosed herein, the corrosion resistance and fatigue life of the fluid ends can be greatly improved.

EXAMPLES

Example 1
Fatigue Study

[0035] A study was conducted to demonstrate the effect of the three-step treatment process on the fatigue life of a metallic surface. This study consisted of testing carbon steel (AISI 4340) without any surface treatment (sample A) in air and in 15 wt.% HCl and testing carbon steel (AISI 4340) with three coating configurations in 15 wt.% HCl. The three coating configurations were: carbon steel treated with shot peening only (sample B), carbon steel treated with ferritic nitrocarburization and oxidization (sample C), and carbon steel treated with ferritic nitrocarburization, oxidization, followed by shot peening (sample D). The unidirectional fluctuating loading applied on the coupon was based on the stresses experienced by the fluid end intersection. The stress ratio also known as R ratio was 0.1 for the testing. The results of the study are shown in FIG. 7.

[0036] FIG. 7 indicates that carbon steel loses endurance limit when tested in 15% HCl solution irrespective of the treatment methods. Fatigue life improvements are not significant when the carbon steel surface is treated with ferritic nitrocarburizing and oxidization (sample C) or shot peening (sample B) alone. Surprisingly, the fatigue life is significantly improved when the carbon steel surface is treated with all three processes combined in the order of ferritic nitrocarburizing, oxidization, and shot peening (sample D).

[0037] Stresses generated at the intersection bore in a typical well servicing job are about 30 kilopound per square inch (ksi) to 80 ksi depending upon the fracturing parameters such as pressure and bore geometry. The three-step process provides particularly improved protection to the carbon steel in this stress range. For example, when exposed to a cyclic stress of 80 ksi in the presence of 15 wt.% of HCl, a carbon steel Without any surface treatment (control, sample A) fails after about 100,000 cycles. Under the same testing conditions, a ferritic nitrocarburizing and oxidization treated carbon steel (sample C) shows worse performance as compared to untreated carbon steel because the treated carbon steel fails after about 70,000 cycles. Shot peening (sample B) improves the cycles to failure to about 400,000. The carbon steel treated with the three-step process disclosed herein (sample D) represents the most significant improvement in fatigue life as it improves the cycles to failure from about 100,000 cycles (control, sample A) to about 600,000 cycles.

[0038] Similarly, at 60 ksi, the untreated carbon steel (control, sample A) fails after about 250,000 cycles when exposed to 15 wt.% of HCl. A ferritic nitrocarburizing treatment followed by oxidization (sample C) worsens the fatigue performance of carbon steel as the treated carbon steel fails after about 200,000 cycles. Shot peening (sample B) increases the cycles of failure to about 800,000 cycles (3.2 times improvement). However, the three-step process treated carbon steel (sample D) represents the most significant life improvement as it increases the cycles of failure from about 250,000 cycles (control, sample A) to about 2,000,000 cycles, which represents 8 times improvement.

[0039] The fatigue life improvement is even more pronounced at 40 ksi when exposed to 15% HCl. For example, the control (sample A) has cycles to failure of about 800,000. Ferritic nitrocarburizing followed by oxidation (sample C) slightly improves the cycles to failure to about 850,000 and shot peening (sample B) improves the cycles to failure to about 1,500,000 whereas the three-step process (sample D) increases the cycles to failure to about 8,500,000.

Example 2
Corrosion Resistance

[0040] The effect of surface treatment on corrosion resistance was studied. A bare metal without any surface treatment (Sample E), a metal treated with a mechanical surface treatment process alone (Sample F), a metal treated with a thermochemical process alone (Sample G), and a metal treated with a three step process of the disclosure (Sample H) were sub-
3. The method of claim 1, wherein nitrocarburizing comprises heating the metallic surface in a gaseous medium at a temperature of about 800°F. to about 1300°F.

4. The method of claim 3, wherein the gaseous medium comprises ammonia and a carbon source comprising carbon dioxide, carbon monoxide, methanol, methane, ethane, propane, butane, pentane, or a combination comprising at least one of the foregoing.

5. The method of claim 4, wherein the gaseous medium further comprises nitrogen.

6. The method of claim 1, wherein forming an oxide layer comprises oxidizing the nitrocarburized surface with air, steam or warm, moist air for about 1 to about 4 hours at about 400°F. to about 600°F.

7. The method of claim 1, further comprising treating the nitrocarburized surface with a sealant, an oil, or a combination comprising at least one of the foregoing.

8. The method of claim 1, further comprising treating the oxide layer with a sealant, an oil, or a combination comprising at least one of the foregoing.

9. The method of claim 1, wherein the mechanical deformation process comprises shot peening.

10. The method of claim 9, wherein shot peening comprises projecting shot materials onto the metallic surface after the oxide layer is formed, wherein the shot materials comprise metallic particles, glass beads, ceramic materials, or a combination comprising at least one of the foregoing.

11. The method of claim 1, wherein the metallic surface comprises steel.

12. The method of claim 1, wherein the metallic surface comprises carbon steel.

13. The method of claim 1, wherein the article is a piston, plunger, pipe, steel ball, steel ball bearing, a fluid end, or a component of a fluid end assembly.

14. An article comprising a treated metallic surface, the treated metallic surface comprising: a diffusion layer and a compound layer from a nitrocarburization process, and an oxide layer from an oxidation process; wherein a compression stress layer and a tensile stress layer from a mechanical deformation process are present in the treated metallic surface.

15. The article of claim 14, wherein the diffusion layer has a thickness of greater than about 100 microns.

16. The article of claim 14, wherein the compound layer has a thickness of about 5 to about 25 microns.

17. The article of claim 14, wherein the oxide layer has a thickness of about 0.2 to about 2 microns.

18. The article of claim 14, wherein the treated metallic surface further comprises at least one of a sealant or an oil.

19. The article of claim 14, wherein the article is a piston, plunger, pipe, steel ball, steel ball bearing, a fluid end, or a component of a fluid end assembly.

20. An article comprising a surface treated according to the process of claim 1.