Bull. Mater. Sci., Vol. 34, No. 1, February 2011, pp. 153–159. © Indian Academy of Sciences.

Plasma nitriding of AISI 52100 ball bearing steel and effect of heat treatment on nitrided layer

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MS received 26 April 2010; revised 6 August 2010

Abstract. **In this paper an effort has been made to plasma nitride the ball bearing steel AISI 52100. The difficulty with this specific steel is that its tempering temperature (∼170–200°C) is much lower than the standard processing temperature (∼460–580°C) needed for the plasma nitriding treatment. To understand the mechanism, effect of heat treatment on the nitrided layer steel is investigated. Experiments are performed on three different types of ball bearing races i.e. annealed, quenched and quench-tempered samples. Different gas compositions and process temperatures are maintained while nitriding these samples. In the quenched and quench-tempered samples, the surface hardness has decreased after plasma nitriding process. Plasma nitriding of annealed sample with argon and nitrogen gas mixture gives higher hardness in comparison to the hydrogen–nitrogen gas mixture. It is reported that the later heat treatment of the plasma nitrided annealed sample has shown improvement in the hardness of this steel. X-ray diffraction analysis shows that the dominant phases in the plasma nitrided annealed sample are ε ($Fe_{2-3}N$) and γ (Fe_4N), whereas in the plasma nitrided annealed sample with later heat treatment only α-Fe peak occurs.**

Keywords. **Plasma ion nitriding; bearing steel; tempered martensite microstructure; toughness; microhardness.**

1. Introduction

Ball bearing steel is also commonly known as WS 1·3505, EN 100 Cr 6, AISI 52100, AFNOR 100 C 6, CCR-1150 and En31 steel. AISI ball bearing steel hardened and tempered with spheroidized carbides is the most commonly used material for bearing applications in rotating devices, machines and automobiles (Basu *et al* 2007). The worldwide popularity of this steel in the above applications arises from the attractive combination of low cost, high hardenability, high yield/tensile strength and good machinability and formability (Hoo 1993). However, high abrasion/wear enhances friction, generates noise/vibration and necessitates an early replacement, which causes premature failure. To meet these great expectations, researchers have been constantly exploring new bearing designs or refining existing ones, optimizing microstructures and chemistry of bearing materials, and alternatively they have been considering the use of thin hard coatings for improved bearing performance and durability applications (Ali 1999). Use of surface hardening has made it possible to produce various steels to exhibit stable quality, high wear resistance reliability and longevity during service in various media.

Many conventional methods for surface modification like gas nitriding (Mirdha 2007), liquid nitriding (Davis 2002) and chrome plating (Morkhov and Egorova 1965) are available in the market. But all these techniques are avoided because they are polluting the environment. Plasma nitriding is another surface hardening technique which has been receiving great attention now a days due to its reduced distortion and the fact that it is an environment-friendly technology (Insup and Ikmin 2007). The plasma nitriding is a thermochemical process to improve the surface properties, such as surface hardness, wear resistance, corrosion resistance, and fatigue strength of various engineering steel components (Hoppe 1998; Podgornik *et al* 1998; Bell *et al* 2000; Borgioli *et al* 2002). Plasma ion implantation has been used to enhance the wear resistance, surface hardness and service life of the bearing steels (Zaitsev *et al* 1990; Blawert *et al* 1996).

To the best of our knowledge, no efforts have been made so far to plasma nitride the AISI 52100 steel. In fact, the plasma nitriding is carried out usually on a quenched and tempered material at temperature around 460–580°C, and also process temperature is kept ∼50°C lower than that of the tempering temperature. AISI 52100 ball bearing steel is not very much suitable for standard plasma nitriding process because this steel is tempered at temperature ∼170–200°C, which is much lower than the standard processing temperature needed in the plasma nitriding treatment. This could be the cause for

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restricted plasma nitriding of this specific ball bearing steel by conventional plasma nitriding mechanism.

In the present work, an effort has been made to plasma nitride the ball bearing steel (AISI 52100) for higher hardness unconventionally. We have three different types of plasma nitrided ball bearing races, i.e. annealed, quenched and quench-tempered samples along with different plasma process temperatures and gas compositions. In quenched and quench-tempered samples, after plasma nitriding process, surface hardness has decreased. We have then focused only on annealed samples. Improved results are obtained on annealed sample after plasma nitriding and its later heat treatment. The obtained results are described in the subsequent sections. The details of the sample preparation and the experimental set up are described in § 2. The results and discussion are presented in § 3, whereas § 4 contains the conclusions.

2. Experimental

2.1 *Sample preparation and detail of samples*

Materials used for assessment in this study were commercially available AISI 52100 bearing steel races. The chemical composition of this standard steel is given in table 1. Ball-bearing races of diameters ranging from 7–15 cm made of AISI 52100 steel were used in the present study. Before plasma nitriding, heat treatments were carried out on three types of ball-bearing steel races as listed in table 2. To observe the temperature effect on the annealed sample it was also heat-treated (i.e. quench-tempered) after plasma nitriding. The process for quenching and tempering was similar as given in table 2. Different samples were prepared by polishing with SiC emery papers of 240, 320, 400, 600 grit size followed by 1 μm diamond paste and alumina paste of 0·05 μm grain size. After polishing, the prepared samples were rinsed with acetone, washed and dried.

2.2 *Plasma nitriding experimental set up*

Plasma nitriding was carried out in large working volume (800 mm diameter and 800 mm height) plasma nitriding system with necessary arrangements of vacuum system and auxiliary heating. A schematic diagram of the plasma ion nitriding system is shown in figure 1. The chamber was evacuated up to a base pressure of 5×10^{-3} mbar with the help of rotary and root pumps. The samples were cleaned before plasma nitriding with argon and hydrogen gas at a ratio of 1:4 and at a pressure of 1 mbar. The gas pressure was measured by Beratron gauge. At this working pressure, 30 kHz pulse d.c. power source was used to ignite the plasma. The argon–hydrogen plasma removed the contaminants from the surface during the cleaning process. After an hour, plasma nitriding process was carried out in the nitrogen–hydrogen and argon–nitrogen gas environments. The typical working pressure was ∼3–5 mbar. The process parameters like process temperature, working pressure and concentration of gas mixtures were varied during the nitriding process and are given in table 3.

Table 1. Chemical composition of AISI 52100 bearing steel in (wt %).

C	Cr	Mn	P	Si	S	Mo	Cu	Ni	Fe
0·98–1·1	1·3–1·6	0·25–0·45	0·025	0·15–0·35	0·020	0·05	0·25	0·25	Balance

Table 2. Different heat-treatments carried out on ball bearing steel races.

Treatment type	Designation	Conditions	Microstructure	Initial hardness
Annealed	A	Heating, 820°C for 4 h 710°C for 10 h 680°C for 2 h Cooling in furnace, till 500°C Cooling in air, till room temperature	Spheroidized carbides	262 HV
Quenched	Q	Heating: ∼850°C Soaking time: 1 h Quenching: oil	Martensite, retained austenite and carbides	874 HV
Tempered	T	Heating: 170–200°C Soaking time: 90 min Cooling: up to room temperature	Tempered martensite, retained austenite and carbides	700 HV

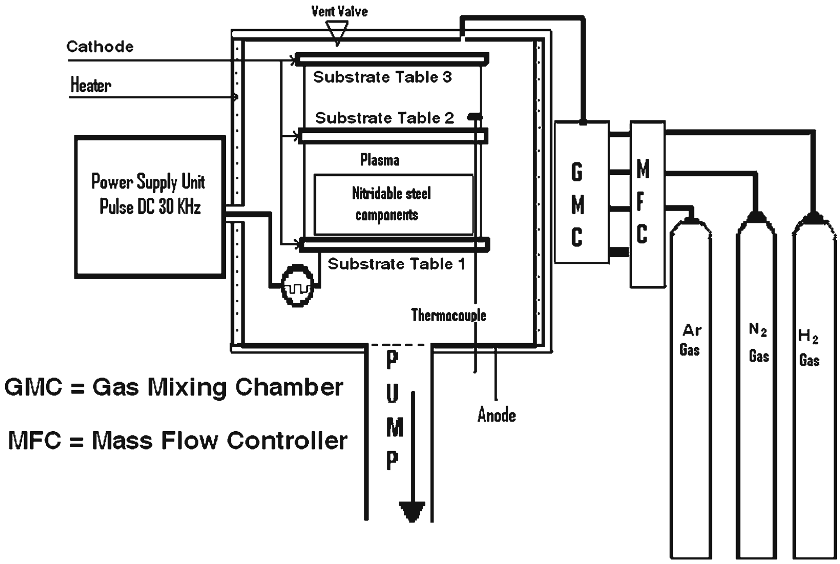

Figure 1. Block diagram of the plasma nitriding system.

2.3 *Characterization techniques used*

Microhardness measurements were performed on the surface of untreated, plasma-nitrided and heat-treated samples surface with a Leitz Vickers Hardness tester using a load of 100 g and a dwell time of 20 s. Case depth of the modified layer was examined by Clemex Meophot-32 make optical microscope at a magnification of 200× and 1000×. The depth of modified layer was measured under the optical microscope by etching the samples with 2% nital. X-ray diffraction (XRD) was used in powder mode. Seifert-made XRD-3000 PTS diffractometer with Cu anode X-ray at 40 kV and 30 mA for Cu Kα radiation ($\lambda = 1{\cdot}5418$ Å) was used. The diffraction patterns were obtained in the 2θ ranges of 30–90° with a step size of 0·1° and counting time of 3 s per step.

3. Results and discussion

3.1 *Effect of process temperature on hardness*

The effect of the process temperature on the hardness of AISI 52100 steel subjected to different heat treatments is shown in figure 2. In this figure the microhardness measurements indicate that the hardness of the samples in annealed condition has increased from 262 HV to 268 HV and 585 HV when plasma nitriding process temperatures are kept at 500°C and 570°C, respectively. The increase in the hardness at high temperature is observed which is attributed by the presence of iron-nitrides formed and also due to the readjustment of the lattice structures. The presence of iron-nitrides is observed in the XRD pattern. On the other hand, there is a reduction in the hardness for the quenched and quench-tempered samples after plasma nitriding. The overall hardness of this steel has reduced to ∼400–500 HV from bulk hardness ∼700 HV at the same processing temperatures of 500°C and 570°C. This could be due to the coarsening of carbides, recovery of dislocation structure and growth of ferrite grains (Mahboubi *et al* 1995). In fact, precipitates with a certain size and number are the most effective in obstructing the movement of dislocations and in producing the maximum strengthening and hardness. At a higher nitriding temperature the precipitate particles are larger in size and more prone to coarsening, leading to a lower precipitate density and hence lower hardness. Softening of the substrate at the higher nitriding temperature may be attributed to coarsening of carbides, recovery of dislocation structure and growth of ferrite grains present in the as-received condition (Mahboubi *et al* 1995).

Table 3. Process parameters for plasma nitriding of AISI 52100 steel.

Expt. No.	Temperature (°C)	Pressure (mbar)	Gas (%)	Time duration
1	560–570	5	65 : 35 (N_2:H_2)	24 h
2	560–570	5	95 : 5 (N_2:H_2)	24 h
3	500	5	95 : 5 (N_2:H_2)	24 h
4	580	3	25 : 75 (N_2:H_2)	4 h
5	580	3	25 : 75 (N_2:Ar)	4 h

3.2 *Effect of gas composition on hardness*

It is clear from § 3·1 that the surface hardness of AISI 52100 steel increases, after plasma nitriding, only on annealed samples. Therefore, we explored the annealed samples and tried to observe the effect of the gas compositions. Figure 3 shows the effect of the gas compositions on the hardness after plasma nitriding process of the annealed samples. It is

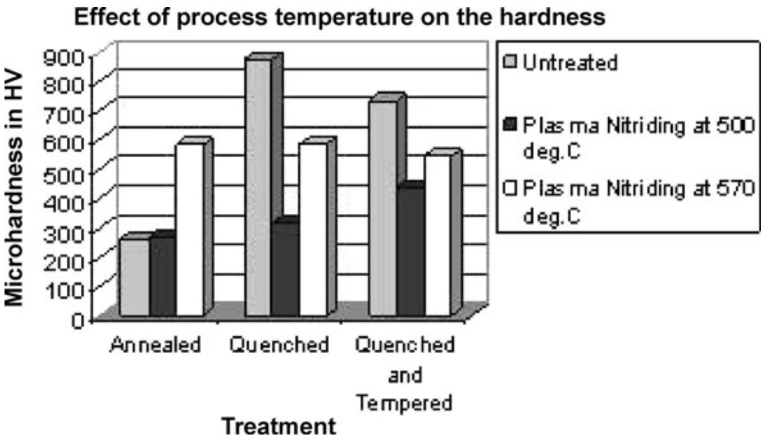

Figure 2. Effect of the process temperature on the hardness of AISI 52100 steel subjected to different heat treatments. Shaded bar shows the hardness of untreated samples, dark bar shows the hardness of plasma nitrided samples at 500°C and bright bar shows the hardness of the plasma nitrided samples at 570°C.

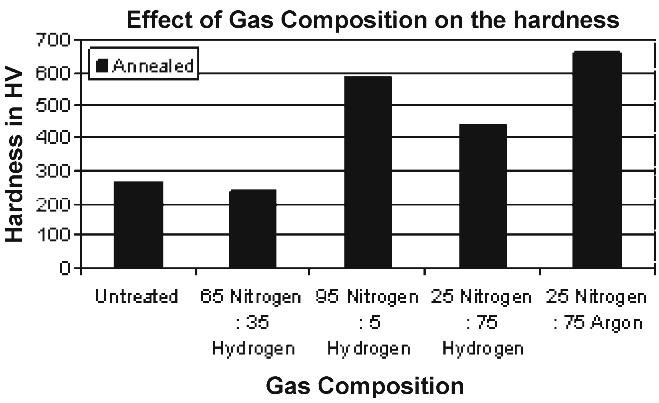

Figure 3. Effect of gas compositions on the hardness of AISI 52100 steel in annealed condition treated at different temperatures and time as listed in table 3.

observed that the surface hardness has increased to ~585 HV from 262 HV when sample is plasma-nitrided with 95% nitrogen and 5% hydrogen gas. The increase in hardness is due to a greater degree of nitrogen dissolution and diffusion, and even precipitation of Fe-nitrides. When sample is plasma nitrided with 25% nitrogen and 75% argon the hardness has increased from 262 HV to 661 HV. The argon gas has higher sputtering yield (Behrisch 1979), and also the argon–nitrogen discharge was found to give higher relative concentration of excited and ionized nitrogen (Meletis and Yan 1993). Due to this fact the presence of argon, instead of hydrogen, should have enhanced the iron nitride compound formation. Furthermore, the gas temperature of discharge generally increases as percentage of Ar in argon–nitrogen mixture increases (Narendra *et al* 2004), so Ar gas can also be considered as a good reagent for increasing temperature of the discharge and hence a better control on the sample temperature. Hence the dissociation of these compounds at higher temperatures on the surface might have allowed higher hardness and increased case depth in the argon–nitrogen gas mixture. The presence of argon in low-pressure plasma nitriding discharge has, however, been reported to improve hardness and it may be beneficial in controlling white layer effects and/or modifying surface morphology (Fancey *et al* 1995).

3.3 *Metallurgical studies*

The untreated annealed AISI 52100 steel showed the spheroidized carbides structure under the optical microscope as shown in figure 4. After plasma nitriding of the annealed

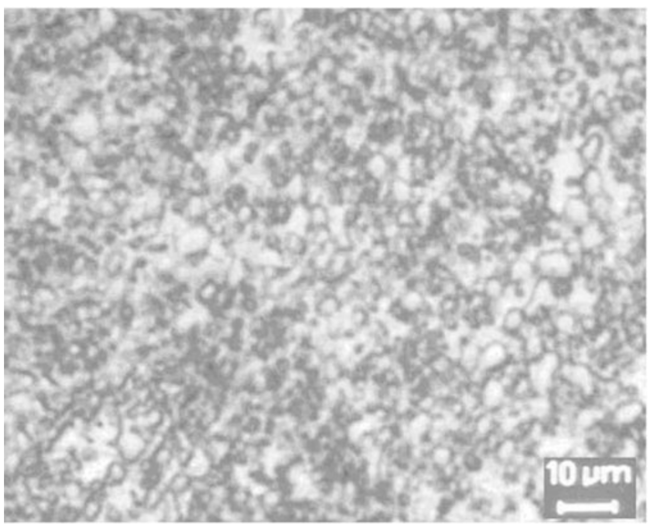

Figure 4. Microstructural view of untreated annealed sample at 1000 magnification.

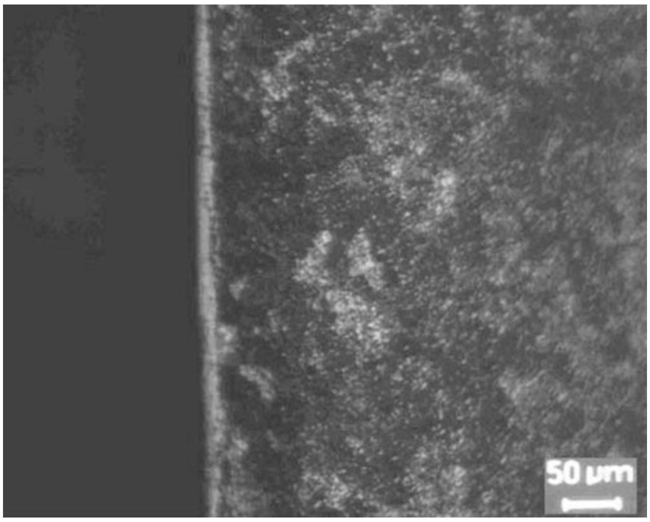

Figure 5. Microstructural view of plasma nitrided annealed sample for 25% nitrogen and 75% argon gas compositions and at 200 magnification.

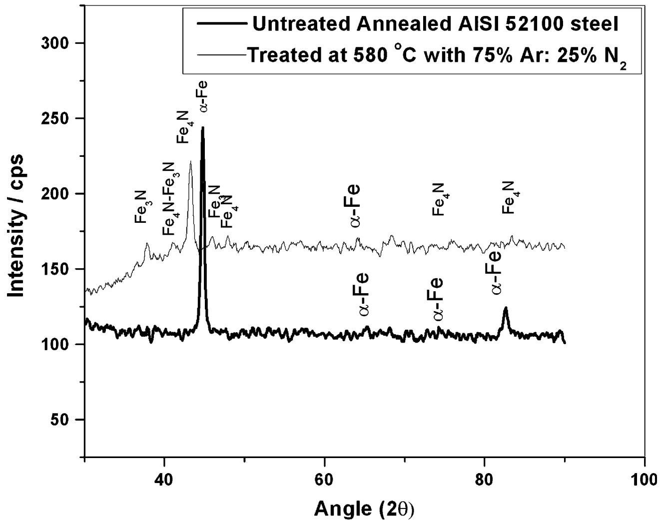

Figure 7. XRD pattern of untreated and plasma treated annealed sample.

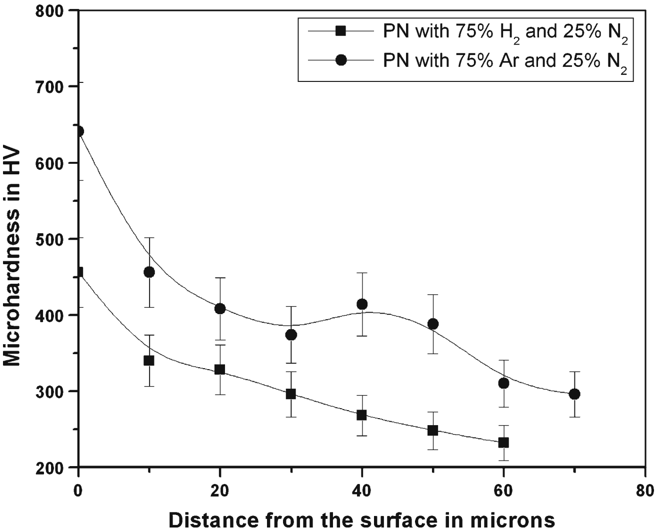

Figure 6. Microhardness depth profile of plasma nitrided annealed samples with different gas compositions.

sample, a cross-section piece of the sample is taken and polished metallographically to observe it under the optical microscope. Plasma nitriding of annealed AISI 52100 sample with 25% nitrogen and 75% argon showed a 7 μm thick white layer and 60 μm diffusion zone (see figure 5). For 25% nitrogen and 75% hydrogen treated sample, 5 μm white layer and 30 μm diffusion zone are found. The white layer is due to the presence of γ-Fe_4N and ε-Fe_3N phases. The effective case depth of 60 μm is also evident from the microhardness depth profile measurement (see figure 6). In this case the hardness is measured after every 10 microns from the surface towards the core, which includes white layer. It is evident from figure 6 that argon and nitrogen combination for AISI 52100 steel produces slightly larger hardness in comparison to the hydrogen–nitrogen gas combination.

X-ray diffraction analysis is also carried out to identify phases formed on the surface before and after the plasma nitriding process. The observed peaks on untreated and plasma-treated annealed sample are shown in figure 7. The untreated sample showed broadened ferrite peaks, whereas plasma nitriding led to the formation of iron nitride precipitates like Fe_4N and Fe_3N and their relative abundance depends on the treatment temperature. Since the chromium nitride peaks are absent, the chromium content of this steel is too low to form a significant amount of hard chromium nitrides. This might be the reason for lower hardness in the annealed samples.

3.4 *Effect of heat treatment on annealed samples after plasma nitriding*

As explained earlier, first we nitrided annealed races of AISI 52100 steel with two different gas compositions. It is observed that plasma nitriding with 25% nitrogen and 75% argon gives a case depth of 60 microns, whereas plasma nitriding with 25% nitrogen and 75% hydrogen gives a case depth of 30 microns. The increase in the case depth and increase in the surface hardness is due to the presence of argon gas. To move one step further, these plasma nitrided races have been heat-treated (i.e. quenched and tempered) later. The obtained hardness with distance from the surface for both the cases is shown in figure 8. The figure also shows the difference between the hardness before and after the heat treatment process of plasma nitrided races. The trends of the hardness after heat treatment is different from the nonheat treated plasma nitrided races.

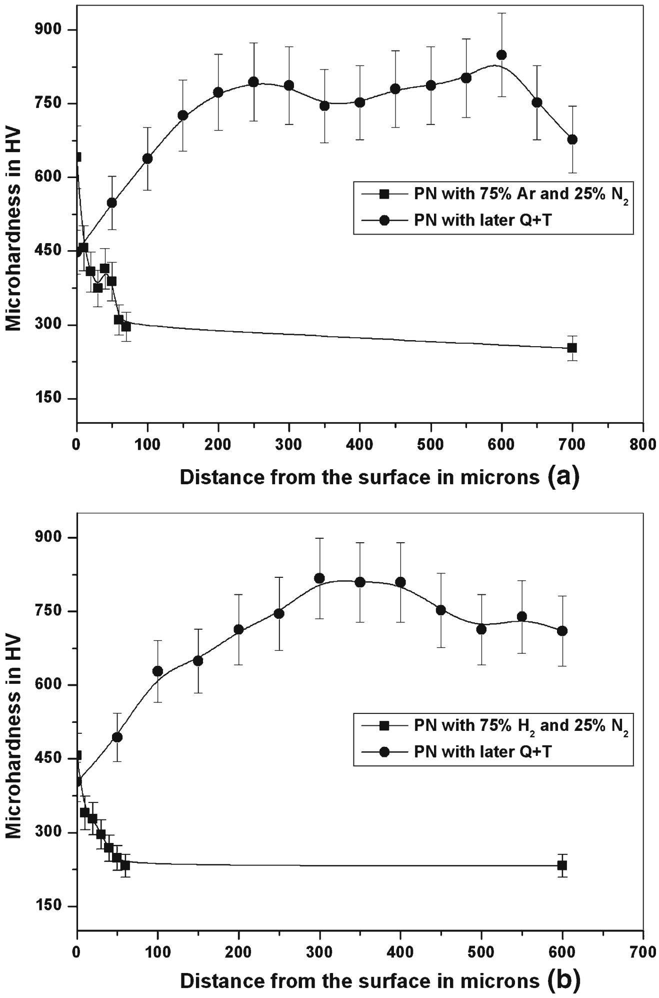

Figure 8. Microhardness depth profile of annealed sample after plasma nitriding and also with later heat treatment. (**a**) 25% Nitrogen and 75% argon gas and (**b**) 25% nitrogen and 75% hydrogen gas.

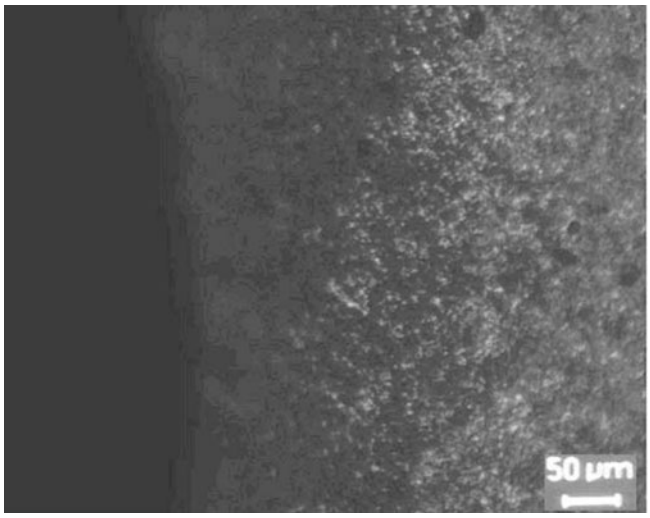

Figure 9. Microstructural view of plasma nitrided annealed sample for 25% nitrogen and 75% argon gas composition and also with later heat treatment at 200 magnification.

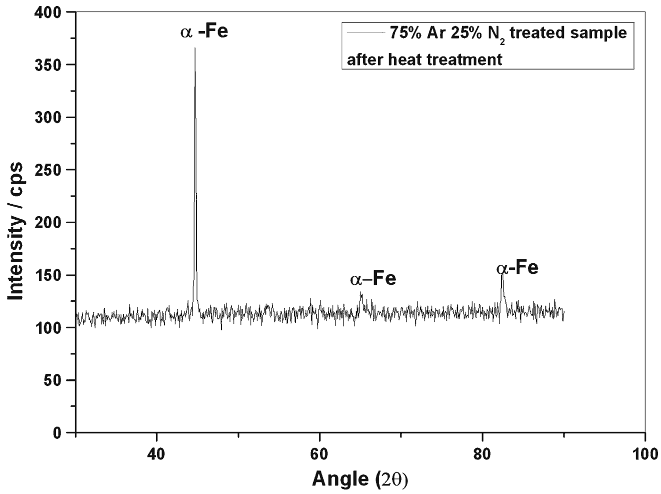

Figure 10. XRD pattern of plasma treated annealed sample with later heat treatment.

The observed trends reveal that after the heat treatment (i.e. quenching and tempering), the surface hardness has reduced in comparison to the plasma nitrided annealed sample without heat treatment. The lower surface hardness (i.e. immediately at the surface) of the nitrided heat treated sample is related to the decrease of nitrogen and carbon contents on the surface during the heat treatment. After certain distance from the surface, the hardness has increased (see figures 8(A) and (B)) indicating the formation of tempered martensite with carbides. The microstructure study of the plasma nitrided and heat-treated samples is shown in figure 9. It indicates that the nitrided layer, which was formed in the nitriding process, has been removed after heat treatment process of the nitrided sample and should have diffused in the depth. The removal of nitrided layer is also confirmed through the XRD analysis. The XRD analysis of the sample after heat treatment has given only α-Fe peaks as shown in figure 10. It also confirms the removal of nitride from the surface that was formed in the nitriding process. As evident from figures 8(A) and (B), with our unconventional procedure we could achieve ~800 HV hardness in around 200–600 μm region below 200 μm from the surface. This hardness region is larger for the samples plasma nitrided with argon–nitrogen gas mixture. This 200 μm layer may be useful for surface finish of the machined sample and the higher hardness region of 250–350 μm could be used to increase the life of the AISI 52100 ball-bearing steel. Our emphasis in this work is to study the case hardened layer after subjecting it to heat treatment process. This step indicates that raising the temperature to higher temperature has removed the nitride layer indicating that there is an outward diffusion of nitrogen and the core got hardened. Hence plasma-nitrided components should not be used at temperatures above 750–800°C.

4. Conclusions

On the basis of the obtained results we can say that it is possible to plasma nitride AISI 52100 steel in the annealed condition. Plasma nitriding of annealed sample is possible at higher temperature (>560°C), whereas on the quenched and quench-tempered samples it reduces core hardness. The argon and nitrogen gas mixture gives higher surface hardness on the annealed samples. On doing quenching and tempering (i.e. later heat treatment) on the plasma nitrided annealed sample, we obtained a region ∼200–600 μm of higher hardness, ∼800 HV below 200 μm region from the surface. The higher hardness region is much better and wider for nitrogen and argon gas-treated samples. The obtained results are promising and a scope exists for further study and also to see the effects on the mechanical behaviour after plasma nitriding of AISI 52100 steel.

Acknowledgements

The authors thankfully acknowledge the Department of Science and Technology (DST), Govt. of India for the financial support for this work under project No. ST(RJ)/DP/2K6/445.

References

Ali E 1999 *Joint tribology conference of the ASME/STLE* (Kissimmee FL)

Basu A, Chakraborty J, Shariff S M, Padmanabham G, Joshi S V, Sundararajan G, Datta Majumdar J and Manna I 2007 *Scr. Mater.* **56** 887

Behrisch R 1979 *Sputtering by particle bombardment I* (Berlin: Springer) p. 47

Bell T, Sun Y and Suhadi A 2000 *Vacuum* **59** 14

Blawert C, Mordike B L, Collins G A, Hutchings R, Short K T and Tendys J 1996 *Surf. Coat. Technol.* **83** 228

Borgioli F, Galvanetteo E, Fossati A and Bacci T 2002 *Surf. Coat. Technol.* **162** 61

Davis J R 2002 *Surface hardening of steels: Understanding the basics* (ASM International)

Fancey K S, Leyland A, Egerton D, Torres D and Matthews A 1995 *Surf. Coat. Technol.* **76–77** 694

Hoo J J C 1993 *Creative use of bearing steels* (West Conshohocken, PA: ASTM International)

Hoppe S 1998 *Surf. Coat. Technol.* **98** 1199

Insup L and Ikmin P 2007 *Mater. Sci. Eng.* **A449–551** 890

Mahboubi F, Samandi M, Dunne D, Bloyce A and Bell T 1995 *Surf. Coat. Technol.* **71** 135

Meletis E I and Yan S 1993 *J. Vac. Sci. Technol.* **11** 25

Mirdha S 2007 *Int. J. Microstruct. Mater. Prop.* **2** 54

Morkhov M I and Egorova K A 1965 *J. Chem. Petrol. Eng.* **1** 144

Narendra J J, Grotjohn T A and Asmussen J 2004 *The 31st IEEE international conference on plasma science* p. 140

Podgornik B, Vizntin J and Leskovsek V 1998 *Surf. Coat. Technol.* **108–109** 454

Zaitsev O V, Kaplun V G, Ivashchuk S V and Filyushin P E 1990 *Met. Sci. Heat Treat.* **32** 650