Improving of shaft steel materials properties using ion nitriding

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Abstract. During operation, shaft steel always contacts with other components, so this material will erode gradually and will be accelerated if this component used in corrosive environment. Finally, the performance of the components to be worse. To improve the quality of the surface components, an ion nitriding technique can be applied. In this research, ion nitriding process was carried out at 300ºC, 350ºC, 400ºC, 450ºC and 1.6 mbar for 4 hours. It can be concluded that generally by increasing the temperature, the hardness increases and at 450ºC reached the highest value in order of 297.86 VHN, while the hardness of raw materials is 98.66 VHN or increases by factors 3, the wear decreases from 60.3 × 10⁻⁹ mm²/kg to 26.8 × 10⁻⁹ mm²/kg or there is an increasing in wear resistance by factor 2.25, and corrosion rate decreases from 4.2465 mpy to 0.6748 mpy. From XRD analysis, it is observed the formed phase are Fe₂N and Fe₃N. The formation of new phase contributes in improving of hardness, wear, and corrosion resistance.

1. Introduction
Ion nitriding is also called plasma nitriding, or glow discharge nitriding or plasma ion nitriding [1], is a process of surface hardening using a glow discharge technology to introduce nascent (elemental) nitrogen to the surface of a metal part for subsequent diffusion into the material [2]. The main purpose of this treatment is primarily used to increase the fatigue strength, wear, corrosion resistance, and surface hardness of steels. Because of the formation of high compressive residual stresses in the case region, increasing surface hardness and case depth cause remarkable improvement in fatigue properties of steels [3].

In plasma DC nitriding process the components to be treated is as a cathode, where the grounded wall of the reactor forms the anode. The treated material is directly involved in the discharge process [4]. Typically, the applied voltage between the anode and the cathode is 400 - 700 Volt. The positive ions produced by glow discharge are accelerated near the cathode surface and bombard the surface of the treated work piece. These ions bombardment heats the workpiece, cleans the surface and provides active nitrogen, and the nitrogen diffusion modifies the surface. During ion nitriding, three reactions will occur at the surface of the material being treated. In the first reaction, iron and other contaminants are removed from the surface of the sample by an action known as sputtering or by a reducing reaction with hydrogen. The impact of hydrogen or argon ions bombarding the sample surface dislodges the contaminants that will be extracted by the vacuum system. The removal of these contaminants allows the diffusion of nitrogen into the surface [5].

In Center for Accelerator Science and Technology, National Nuclear Energy Agency of Indonesia(PSTA-BATAN), the plasma nitriding process was carried out using homemade DC-glow
discharge plasma in which usually used for carburizing and nitrocarburizing processes [6,7,8,9,10]. In this research, the plasma nitriding process was conducted at 300 up to 450°C, 1.6 mbar, and 4 hours of nitriding time. After the treatments, several parameters such as surface hardness, wear rate, corrosion rate, and phase material were tested using Matsuzawa MMT-X7 microhardness tester, Ogoshi High-Speed Universal Wear Testing Machine, potentiostat type PGS-201, and X-Ray Diffractometer (XRD), respectively.

2. Experiment
The schematic representation of plasma nitriding, indicating the different steps in the formation of the nitride film is presented in Figure 1.

![Figure 1. Schematic representation of plasma nitriding, indicating the different steps in the formation of the nitride film [11, 12, 13, 14].](image)

The mechanism of plasma nitriding (Figure 1) is divided into 4 steps, namely (1) the process of ionization of nitrogen atoms, (2) the process of sputter, (3) the process of forming FeN compounds and (4) the process of diffusion [13, 14, 15].

**Step 1.** The ionization process of nitrogen atoms starts from dissociation to the formation of glow discharge plasma, the reaction between electrons and nitrogen molecules to form nitrogen ions as follows: [16]

\[
e + N_2 \rightarrow N + N + e^- \\
e + N \rightarrow N^+ + 2e^- \\
e^- + N_2 \rightarrow N^+ + N + 2e^-
\]

**Step 2.** The surface of the workpiece (steel) is sputtered with nitrogen ions (N+) so that the atoms of surfaces of a steel and impurities are sputtered. The sputtered impurity is removed from the plasma chamber by a vacuum pump and is called atomic surface cleaning.

**Step 3.** The atoms of steel (Fe) to meet with the N atoms to form a FeN unstable compound which is a start of nitriding process.

\[
Fe + N \rightarrow FeN
\]

**Step 4.** The unstable compound FeN condenses on the surface of the workpiece thereby releasing nitrogen atom and forming lower-order iron nitrides, Fe2N, Fe3N and Fe4N. As a result of this reaction, the released nitrogen atoms will diffuse into the material to form a new compound diffusion zone as follows:

\[
FeN \rightarrow Fe_2N + N
\]
The material for this research was a shaft steel material with chemical compositions consist of 98.46%, 0.245%, 0.286%, 0.532%, 0.005%, 0.010%, 0.114%, 0.017%, 0.050%, 0.071%, 0.004%, 0.01% of Fe, C, Si, Mn, P, S, Cr, Mo, Al, Cu, Sn, and V, respectively. The shaft materials in the rod form was cut into 3 × 1.4 mm in a disc size. The specimens were grounded with SiC papers from 80 up to 5000 grit and polished mechanically with 1µm diamond paste. The polished specimens were washed with acetone in an ultrasonic cleaner and dried at room temperature.

3. Results and Discussion
In this research, the plasma nitriding process was conducted at 300 up to 450ºC, 1.6 mbar, and 4 hours of nitriding time. After the treatments, several parameters such as surface hardness, wear rate, corrosion rate, and phase material were tested.

3.1. Hardness and wear test
The effects of temperature on the hardness and wear of shaft steels materials treated at p = 1.6 mbar, t = 4 hours and the temperature varied from 300 up to 450ºC are shown in Figures 2 and 3.

\[
Fe_2N \rightarrow Fe_3N + N \text{ (ε phase)} \tag{6}
\]

\[
Fe_3N \rightarrow Fe_4N + N \text{ (γ’ phase)} \tag{7}
\]

\[
Fe_4N \rightarrow Fe + N \tag{8}
\]

Figure 2. Effect of temperature on the hardness of ion nitrided shaft steel material at 1.6 mbar and 4 hours of nitridation process.

Figure 3. Effect of temperature on the wear rate of ion nitrided shaft material steel at 1.6 mbar and 4 hours of nitridation process.
Figure 2 shows the increasing of surface hardness with an increase in nitriding temperature. The reason for this phenomenon can be explained such as follow: by increasing the temperature, the solubility limit of nitrogen in the solid increase and also the possibility formation of compound layer on the surface after the solubility limit of nitrogen in the solid solution also increase [17,18,19]. The formation of compound creates the formation of high compressive residual stresses. This is also evident from XRD analysis presented in Figure 6, which is observed the formation of Fe\(_2\)N, Fe\(_3\)N compound. This phenomenon, cause remarkable improvement in the mechanical properties. Based on wear test data presented in Figure 3, the wear rate decreases from \(60.3 \times 10^{-9} \text{ mm}^3/\text{kg mm} \) to be \(26.8 \times 10^{-9} \text{ mm}^3/\text{kg mm} \) or reducing in wear rate by factor 2.25. Based on hardness and wear rate test presented in Figures 2 and 3 shows that wear rate is inversely proportional to the hardness or wear rate is directly proportional to the hardness.

3.2. Corrosion Test

Corrosion test results for raw material and nitrided material at 400°C of temperature, 1.6 mbar and 4 hours of duration time of process are presented in Figures 4 and 5 respectively. From this data, it can be seen that for raw material, the current corrosion density \(I_{\text{corr}} = 9.475 \mu\text{A/cm}^2\), or after calculating, for value of \(I_{\text{corr}} = 9.475 \mu\text{A/cm}^2\) will give a corrosion rate (CR) is 4.24658 mpy, while after being nitrided at 450°C, 1.6 mbar and 4 hours of duration of process, the current density \(I_{\text{corr}} = 1.509 \mu\text{A/cm}^2\) or CR is 0.6748 mpy. From this data also can be seen that nitrided sample has lower current density \(I_{\text{corr}}\) than un-nitrided sample or raw material. The nitride sample also has more positive of corrosion potential \(E_{\text{corr}}\) than un-nitrided sample. From this data can be concluded that effect of nitriding process can reduce the corrosion rate by factor 6.3, or in other hand effect of plasma nitriding process can increase the corrosion resistance of the material. The improvement of the corrosion resistance is due to the formation of new phase iron nitride of Fe\(_2\)N and Fe\(_3\)N and iron carbide such as Fe\(_3\)C and also iron oxide such as FeO\(_2\) and Fe\(_2\)O\(_4\). The formation of new phase is indicated by the data from XRD analysis presented in Figure 6.

![Figure 4](image1.png) Raw material, \(I_{\text{corr}} = 9.475\mu\text{A/cm}^2\) or CR = 4.24658 mpy.

![Figure 5](image2.png) Ion nitrided shaft steel treated at 1.6 mbar, 450°C for 4 hours, \(I_{\text{corr}} = 1.509\mu\text{A/cm}^2\) or CR = 0.6748 mpy.
3.3. Phase analysis
The formation of new phases was analyzed using XRD. Figure 6 shows the diffraction pattern of raw material and ion nitrided shaft steel treated at 1.6 mbar for 400°C and 450°C. From the experimental data and then was analyzed using data database Crystallography Open Database (COD) from program Match 2. From 2-theta experimental data is then matched with 2-theta data base and also calculation theoretically, so it can be found the formed phases. It can be analyzed that the formed phases are Fe₂N, Fe₃N, Fe₃C, FeO₂ and Fe₂O₃.

![Figure 6. Diffraction pattern of raw material and ion nitrided shaft steel treated at 1.6 mbar at 400°C and 450°C.](image)

4. Conclusion
Based on the experiments carried out, it can be concluded that generally by increasing the temperature, the hardness increase and at 450°C reached the highest value in order of 297.86 VHN, while the hardness of raw materials is 98.66 VHN or increases by factors 3, the wear decreases from 60.3 × 10⁻⁹ mm³/kg mm to 26.8 × 10⁻⁹ mm³/kg mm or there is an increasing in wear resistance by factor 2.25, and corrosion rate decreases from 4.2465 mpy to 0.6748 mpy. From XRD analysis, it is observed the formed phase are Fe₂N, Fe₃N, Fe₃C, FeO₂ and Fe₂O₃. It can be concluded that the main contribution in improving in hardness, wear and corrosion resistance is caused by the formation of new phase namely; Fe₃C, F₂O₃ and FeO₂.

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