Evaluation of the Gas Nitriding of Fine Grained AISI 4135 Steel Treated with Fine Particle Peening and Its Effect on the Tribological Properties

Shoichi Kikuchi¹,* and Jun Komotori²

¹Department of Mechanical Engineering, Faculty of Engineering, Kobe University, Kobe 657-8501, Japan
²Department of Mechanical Engineering, Faculty of Science and Technology, Keio University, Yokohama 223-8522, Japan

The effect of fine particle peening (FPP) on the gas nitriding of AISI 4135 chromium-molybdenum steel was investigated. Surface microstructures of nitrided specimens pre-treated with FPP were characterized using scanning electron microscopy (SEM), X-ray diffraction (XRD), and glow discharge optical emission spectroscopy (GDOES). The nitrided layer formed on the fine ground specimen treated with FPP was thicker than that on the nitrided-only specimen, because the fine grains created by FPP accelerate the formation of iron nitride during the nitriding process. Furthermore, FPP reduces the concentration of chromium near the nitrided surface, which suppresses the formation of cracks and pores in the compound layer. Therefore, a nitrided specimen pre-treated with FPP has higher hardness than a nitrided-only specimen.

Reciprocating ball-on-disk friction tests were performed at room temperature to investigate the tribological properties of the nitrided AISI 4135 steel. The nitrided specimen pre-treated with FPP had a lower friction coefficient and exhibited less wear loss due to the presence of a thick compound layer without cracks and pores. Therefore, a hybrid surface modification that employs FPP as a processing step prior to gas nitriding is effective for improving the tribological properties of AISI 4135 steel.

Keywords: nitriding, shot peening, grain refinement, wear, friction, diffusion

1. Introduction

Gas nitriding has been widely used in various fields of engineering to improve the fatigue strength and wear resistance of metallic materials used for mechanical components. This process can increase hardness and generate compressive residual stress on the surface of the material.¹⁻⁶ Gas nitriding also allows precise control of the chemical potential of nitrogen in the process environment and typically enables to be performed for steels at a lower temperature (around 800 K), which results in the formation of high-purity nitrides.

The surface-modified layer created by the nitriding process generally consists of two types of layers; a compound layer on the top surface and a diffusion layer beneath it. The compound layer especially improves the tribological properties of a material due to its high hardness;⁴⁻⁸ however, in some cases, it also reduces the fatigue strength of the material²⁻⁵⁻⁹ due to its brittleness and the presence of cracks and pores. Therefore, the compound layer is removed by grinding and blasting processes to prevent the nitrided products from decreasing the fatigue strength, although it exhibits high wear resistance. It is necessary to achieve both higher fatigue and wear resistance of nitrided steels.

We have previously proposed a hybrid surface modification using fine particle peening (FPP) as a pre-processing step to gas nitriding⁵⁻⁷⁻¹⁰ for modifying the microstructure of the compound layer. The mechanism of pore formation in the compound layer is related to the microstructural change and metastability of nitrides during nitriding;¹¹⁻¹³ therefore, we have focused on grain refinement by FPP, which enables to change the elemental diffusion behavior.¹⁴⁻¹⁶ The dislocation density and the grain size are important factors that enhance the nitrogen diffusion behavior.⁴⁻⁷⁻¹⁷⁻²¹ For example, Wroblewski and Skalski,¹⁷ and Tong et al.,¹⁴⁻¹⁸ reported that the nitrogen diffusion behavior was significantly enhanced for fine grained pure iron after shot peening. The FPP treatment highlighted in this study can create finer crystal grains within a short time²²⁻²⁸ because the particle velocity obtained with FPP is higher than that with conventional shot peening.²³ We have reported that the fatigue strength of nitrided AISI 4135 chromium-molybdenum steel pre-treated with FPP was improved due to the formation of a dense compound layer.⁹ This dense compound layer is also expected to improve the wear resistance of steel; however, the mechanism for the formation of this dense compound layer and the effect of the layer on the tribological properties have not yet been investigated.

The aims of this study are to characterize the nitrided layer formed on fine grained AISI 4135 steel pre-treated with FPP and to clarify the effect of the nitrided layer on the tribological properties of AISI 4135 steel.

2. Experimental Procedure

2.1 Specimen preparation

The material used in this study was AISI 4135 chromium-molybdenum steel with the chemical composition shown in Table 1. This steel contains chromium, which can precipitate as nitrides. Steel rods (15 mm diameter) were machined into 4 mm thick disks, polished with emery papers (#320 to #1200), and then mirror-finished using SiO₂ suspension. The polished specimens were annealed at 1373 K for 2 h (A series) in vacuum to remove strain induced by the machining and polishing processes. Figure 1 shows an optical micrograph of the A series etched with a 3% Nital solution.

Table 1 Chemical composition of AISI 4135 chromium-molybdenum steel (mass%).

<table>
<thead>
<tr>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Cu</th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34</td>
<td>0.24</td>
<td>0.81</td>
<td>0.011</td>
<td>0.018</td>
<td>0.02</td>
<td>1.11</td>
<td>0.16</td>
<td>0.01</td>
<td>0.026</td>
<td>Bal.</td>
</tr>
</tbody>
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*Corresponding author, E-mail: kikuchi@mech.kobe-u.ac.jp
Figure 2 shows a flowchart that illustrates the specimen preparation procedures; five types of specimens were prepared with different surface-modified layers. FPP was performed under the conditions given in Table 2. Table 3 and Fig. 3 show the chemical composition and a scanning electron microscopy (SEM) micrograph of the shot particles used in this study, respectively. The shot particles (63 µm diameter) were prepared from high-speed tool steel (M42 steel) with a Vickers hardness of 876 HV. After FPP treatment, gas nitriding was performed at 823 K for 6 h in a nitrogen and ammonia environment (F+N series) at atmospheric pressure. Partial pressure of a nitrogen and ammonia gases was 30.2 kPa and 71.1 kPa, respectively. In addition, the specimens treated only with FPP (F series), nitrided specimens (N series) and the specimen treated with FPP after nitriding (N+F series) were prepared.

2.2 Characterization of the surface-modified layer

The hardness distributions of the surface-modified specimens were measured along the cross section of the specimens using a micro-Vickers hardness tester at a load of 0.245 N. The surface microstructure of the modified specimens was characterized using SEM and glow discharge optical emission spectroscopy (GDOES). The crystal structures of the specimens were identified using X-ray diffraction (XRD) with Cu Kα radiation (wavelength: 0.154 nm).

2.3 Evaluation of the tribological properties of nitrided steel pre-treated with FPP

Reciprocating ball-on-disk dry friction tests were performed at room temperature to investigate the tribological properties of the nitrided specimens. A 10 mm diameter ball of high wear resistance alumina was used to evaluate the wear behavior of the nitrided substrates. The nominal applied force was 9.8 N, the sliding distance was 32000 mm, the sliding stroke was 8 mm, and the speed was 5 mm/s. The frictional force was measured when the reciprocating ball was moving in the forward direction to determine the friction coefficient. The amount of wear loss during the reciprocating friction tests was also measured using an electric balance. After testing, the worn surfaces of the specimen and the alumina ball were examined using SEM and a non-contact scanning white light interferometer.

3. Results

3.1 Characterization of FPP-treated surface

Figure 4 shows cross-sectional SEM micrographs of the annealed specimen (A series) and FPP-treated specimens (F series) etched with Nital solution. A stratification-patterned layer was evident at the FPP-treated surfaces, as indicated by dotted lines in Figs. 4(b), 4(c) and 4(d). The thickness of the layer structure increased with peening time. Figure 5 shows typical features of the stratification-patterned layer observed using high magnification SEM with angle selective backscattered electron detector after glow discharge etching. Figure 5(a) shows that the stratification-patterned layer contains finer grains than the surrounding structure. Moreover, lamellar structures were observed around the stratification layer structure and the space between lamellar structures was approximately 170 nm (Fig. 5(b)).

XRD analysis was conducted to examine the characteristics of the microstructure of the F series in more detail. Figure 6 presents the relationship between the peening time...
and the full width at half maximum (FWHM) of the $\alpha$-Fe (110) XRD peak. The FWHM of the F series tended to increase with increasing peening time. This is because the total kinetic energy of the shot particles increases with peening time.24) These results confirm that FPP forms a stratification-patterned microstructure that contains fine grains near the surface of AISI 4135 steel.

### 3.2 Characterization of nitrided layer formed on the fine grained steel pre-treated with FPP

Figure 7 shows the distribution of Vickers hardness at various cross-sectional depths. FPP and nitriding increased the surface hardness of the specimens and the F+N series, which was treated with both FPP and nitriding, had higher hardness than the nitrided-only specimen (N series). In addition, the thickness of the nitrided layer on the F+N series was larger than that on the N series.

The microstructures of the nitrided layers were observed using SEM to clarify the reason for the higher hardness in the F+N series. Figures 8 and 9 show SEM micrographs that indicate the typical microstructural features of the N and F+N series after glow discharge etching, respectively. The compound layer could be observed near the surfaces of both specimens. In the case of the N series (Fig. 8), a porous region and crack were observed inside the compound layer, whereas the F+N series did not have these features (Fig. 9), which is why the F+N series exhibited higher hardness than the N series.

Thus, the fine grains created by FPP influence the microstructure of the nitrided layer on AISI 4135 steel, resulting in the formation of a thick and hard compound layer without cracks and pores.

### 3.3 Evaluation of the tribological properties of nitrided steel pre-treated with FPP

Reciprocating friction tests were performed to investigate the tribological properties of the nitrided AISI 4135 steel pre-treated with FPP. Figure 10 shows the relationship between the friction coefficient and the number of sliding cycles, and...
the sliding distance. The friction coefficient of the N series was suddenly increased after 50 sliding cycles. Alsaran reported that a brittle compound layer failed in the initial period of sliding with high stress, which with the present results suggests that the compound layer on the N series surface may fail due to the presence of cracks and pores during tests.

In contrast, the friction coefficient of the F+N series remained lower than that of the N series over the entire test period. The tribological properties of the N+F series were also investigated for comparison with the F+N series. The N+F series did not contain cracks and pores inside the compound layer because FPP removed them in the compound layer. The friction coefficient of the N+F series was low in the early period of sliding; however, suddenly increased after 100 sliding cycles and reached almost the same value as the N series. Figure 11 shows the wear loss for the F+N and N+F series during tests. The F+N series showed less wear loss than the N+F series, which suggests that the hybrid surface modification with FPP prior to gas nitriding is effective for improving the tribological properties of AISI 4135 steel.

4. Discussion

4.1 Gas nitriding of fine grained steel pre-treated with FPP

FPP was performed prior to gas nitriding to modify the microstructure of the nitrided layer on AISI 4135 steel. This hybrid surface modification can suppress the formation of cracks and pores inside the compound layer of AISI 4135 steel. In this section, the gas nitriding behavior of the FPP-treated steel is discussed.
Figure 12 shows XRD patterns for the N and F + N series. Both of specimens exhibit diffraction peaks due to α-Fe, iron nitride (Fe₃N) and iron oxide (Fe₃O₄); however, the intensities of the iron nitride (Fe₃N) and ε-Fe peaks were different and dependent on the peening time. Figure 13 shows the relationship between the peening time and the intensities of the Fe₃N(111) and ε-Fe(110) peaks. The intensity of the Fe₃N peak rapidly increased within 1 s of FPP treatment, and then became saturated for longer FPP treatment times. In contrast, the intensity of the ε-Fe (110) peak decreased with increasing peening time and then became saturated. These results indicate that fine grains created by FPP accelerate the formation of iron nitride.

Depth profiles of the elements were then measured using GDOES to examine the characteristics of the nitrided layer in more detail. Figure 14 presents depth profiles of nitrogen and chromium in the N and the F + N series, respectively. The signal intensity on the vertical axis is proportional to the element concentration and the sputtering time on the horizontal axis corresponds to the depth from the surface. Figure 14(a) shows that the N-rich region in the F + N series is thicker than that in the N series, which corresponds to the hardness distribution shown in Fig. 7. In contrast, Fig. 14(b) shows that the Cr-rich region in the F + N series is thinner than that in the N series. XRD and GDOES analyses indicate that the fine grains created by FPP accelerate the formation of iron nitride during the nitriding process, which results in a reduced concentration of chromium near the nitrided surface.

The formation of cracks and pores in the compound layer is related to the metastability of nitrides due to the presence of chromium in the substrate. The authors have reported that the local chromium concentration surrounding the porous region in the compound layer is high. Hosmani et al. reported that pores in the compound layer are formed due to recombination of nitrogen atoms to N₂ during the transformation of the ferrite matrix into iron nitrides surrounding CrN precipitates. On the basis of these reports and the present results, FPP reduces the concentration of chromium in the compound layer created by the subsequent nitriding process, which results in suppressing the formation of cracks and pores inside the compound layer.

4.2 Tribological mechanism of nitrided steel pre-treated with FPP

The use of FPP as a pre-processing step to gas nitriding forms a high hardness layer without cracks and pores, which results in improvement of the tribological properties of AISI 4135 steel. The friction and wear mechanism of a nitrided specimen pre-treated with FPP is discussed here.

Figure 15 shows wear track analysis results for the F + N and N + F series conducted using a non-contact scanning white light interferometer. The wear track on the N + F series
was slightly deeper than that on the F+N series. Moreover, the local surface topography induced by FPP remained concave on the worn surface of the F+N series (Fig. 15(a)), which indicates that peaks on the compound layer are locally worn by contact with the counter material. In contrast, such surface topography was not observed on the worn surface of the N+F series (Fig. 15(b)). This may be because surface roughness $R_a$ of the N+F series ($0.37 \mu m$) was lower than that of the F+N series ($0.72 \mu m$).

The surface of the counter material was also observed using SEM after wear testing to investigate the wear mechanism of both types of nitrided specimens. Figure 16(a) shows that local adhesion of the substrate was observed on the surface of the counter material for the F+N series. In contrast, adhesion of the N+F series substrate was observed over the entire surface of the counter material (Fig. 16(b)). Microstructural observation of the N+F series cross-section revealed that the depth of the wear track was larger than the thickness of the compound layer. These results indicate that the substrate beneath the compound layer is worn and adhesion wear occurs with the N+F series specimen because it has a thin compound layer.

Figure 17 shows a schematic illustration of the surface microstructure and tribological mechanism of the nitrided specimens. For the nitrided-only specimen (Fig. 17(a)), the compound layer fails in the early stage of wear testing due to the presence of cracks and pores; therefore, the N series has a high friction coefficient. When pores in the compound layer are removed by FPP after nitriding (Fig. 17(b)), the friction coefficient is lower during the early stage of wear testing. However, the diffusion layer beneath the compound layer is worn because the compound layer is thin, so that adhesive wear occurs on the surface. Therefore, the N+F series has a relatively high friction coefficient as with the N series and greater wear loss, although the compound layer does not have cracks and pores. In contrast, abrasive wear occurs mainly on the surface of the nitrided specimens pre-treated with FPP (Fig. 17(c)) because the thick and hard compound layer is gradually worn without fracture, therefore, the compound layer remains on the surface of the F+N series after reciprocating friction tests, and a low friction coefficient is maintained with less wear loss than that for the N and N+F series.

Thus, the hybrid surface modification; using FPP as a pre-processing step to gas nitriding enables the formation of a thick compound layer without cracks and pores, which results in improvement of the tribological properties of AISI 4135 steel.

5. Conclusion

Fine particle peening (FPP) was performed prior to gas nitriding to modify the microstructure of AISI 4135 chromium-molybdenum steel. The microstructure of the nitrided steel pre-treated with FPP was characterized, and the effect of this treatment on the tribological properties was investigated. The following conclusions were reached:

(1) Hybrid surface modification using FPP as a pre-processing step to gas nitriding enables the formation of a thick compound layer with high hardness on AISI 4135 steel.

(2) FPP treatment prevents the formation of cracks and pores in the compound layer during the subsequent nitriding process. This is because the stratification-patterned layer, which contains fine grains created by
FPP, accelerates the formation of iron nitride and results in a decreased concentration of chromium.

(3) The nitrided specimen pre-treated with FPP has a lower friction coefficient and less wear loss. The hybrid surface modification improves the tribological properties of AISI 4135 steel due to the presence of a thick and hard compound layer without cracks and pores.

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