Abstract

Pulse laser nitriding of GCr15 steel in the surrounding of NH₃ gas was studied. The experimental results show that a high hardness, good wear resistance, compact and uniformity hard layer of iron nitride was obtained. The results of micro-hardness and wear rate testing shows that after laser nitriding, the micro-hardness of the sample increased 18 percent and wear rate of the sample decreased 50 percent, laser nitriding improves the sample’s wear resistance character. The nitriding layer is about 150μm thick and contains nitrided iron dendrites. The microstructure, phase constitution, micro-hardness, depth and wear character of the nitriding layer were determined and analyzed, and the pulsed laser nitride mechanism on the surface of GCr15 steel was discussed.

Keywords: pulse laser; laser nitriding; GCr15; micro-hardness; wear rate; mechanism of laser nitriding

1. Introduction

GCr15 steel was the common materials, has widely used in rolling bearing, precision measuring tools, frosty die, machine screw, long-life precision moving components. It needs the performance of high hardness and good wear resistance. In particular wear resistance, which has a direct impact on their useful life.

Nitride is the conventional heat treatment method, form a nitrogen levels in the surface layer of workpiece, by this can obtain high hardness and good wear resistance surface. The principle is: the ammonia molecular adsorbed on the surface of workpiece will decompose nitrogen atoms at a high temperature, the nitrogen atoms between the internal and the surface of the workpiece has a large concentration gradient, which in the surface of the workpiece will diffuse to the internal of the workpiece compounded with iron atoms, then forms high hardness nitrides. The specific process is place the workpiece in a vacuum tank, leads to a certain amount of ammonia and then heat the workpiece to the required temperature. Ammonia pressure or flow and the heat preservation time will be set up. Through this technology could obtain high hardness and good wear resistance surface, but require a longer
processing time. Because it is the treatment at the same time to the entire workpiece, therefore, easily lead to deformation of the workpiece and affect its accuracy, therefore, part treatment can not be achieved.

Laser surface nitriding as a new technology compared with the conventional nitriding process has the advantages of fast heating, smaller deformation of workpiece and pollution-free; after treatment the surface has high performances of wear resistance, hardness and fatigue strength; the process is easily to control, Production Automation; particularly suitable for partial nitriding treatment, this is the conventional process can not be compared. The majority reported in the reference is using high-power CW laser surface nitriding, compared with the high-power CW laser using pulsed laser can significantly reduce the heat deformation for small workpiece[1-5].

In this paper, we have studied the GCr15 steel surface nitriding by using pulsed laser, through the characterization and analysis of the surface by laser irradiation, we believe that the modified layer is made of a mixture of Fe2-3N and Fe, and have discussed the mechanism of laser nitriding.

2. Testing materials, equipment and methods

In this experiment, using GCr15 bearing steel as the testing substrate, its chemical composition as shown in Table 1.

<table>
<thead>
<tr>
<th>Constituent elements</th>
<th>C</th>
<th>Ni</th>
<th>Sn</th>
<th>Mn</th>
<th>Cr</th>
<th>As</th>
<th>P</th>
<th>Cu</th>
<th>Si</th>
<th>S</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass fractions/%</td>
<td>1.01</td>
<td>0.12</td>
<td>0.02</td>
<td>0.32</td>
<td>1.17</td>
<td>≤0.04</td>
<td>0.012</td>
<td>0.08</td>
<td>0.21</td>
<td>0.007</td>
<td>0.02</td>
</tr>
</tbody>
</table>

Using cutting machine to cut the substrate into small pieces, the size as 6mm × 7mm × 8mm, polishing and cleaning the surface of the small pieces.

Experimental laser is used as Nd:YAG pulsed laser, its average power is 500W, wavelength is 1.06μm, pulsed width is from 0.5 to 5.0ms adjustable. The Scheme of experimental device has shown in Fig.1.

![Fig.1 Schematic diagram of laser surface nitriding](image)

We chose NH3 as the nitrogen source gas, during the process of testing chemical reaction occurs as following:

\[ \text{NH}_3 \rightarrow 3\text{H} + [\text{N}] \]

\[ x\text{Fe} + [\text{N}] \rightarrow \text{Fe}_x\text{N} \]

Nitriding process is carried out in pressure reaction chamber. After ultrasonic cleaning, placed the GCr15 steel pieces on the samples table, which in the reaction chamber; exhaust make the vacuum degree in chamber to \(10^{-1} \sim 10^{-2}\)Pa, afterward, ventilate NH3 to chamber make the atmospheric pressure reaches 1.0kg/cm². Pulsed laser focused by the lens vertically irradiated to the sample surface through the quartz glass window. Carefully adjust the laser
energy, the distance from lens to the sample and the moving speed of sample table. Through the observation, we found have formed a bright nitrided zone on the surface of the sample.

3. Test Results and Analysis

We have made XRD analysis, surface hardness and hardening depth measurement, surface and profile morphology analysis to the laser-nitrided GCr15 steel samples.

From XRD patterns (as shown in Fig.2) can see that: in the laser-nitrided GCr15 steel surface layer, nitrogen existed as cubic phase of hard compound phase Fe$_{2-3}$N, Fe$_{2-3}$N has high hardness, and it plays a vital role in strengthening the hardened layer. Fe$_{2-3}$N cubic phase content determines the hardness of hardened layer.

Test results of hardness and wear rate of the non-nitrided and nitrided GCr15 steel samples has shown in Table 2, using MH-5 Micro-hardness measuring instrument and MM2000 friction and wear test machine. Take the average of the five times measured value.

<table>
<thead>
<tr>
<th>Sample status</th>
<th>Before treatment</th>
<th>After treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness/HV</td>
<td>447.97</td>
<td>976.00</td>
</tr>
<tr>
<td>Wear rate/$\times 10^{-5}$mm$^3$/m$^\circ$N</td>
<td>3.21</td>
<td>1.59</td>
</tr>
</tbody>
</table>

By the thickness and the wear rate changes of the sample before and after laser treatment can see that, after laser nitrided has highly improved the surface hardness and wear performance of GCr15 steel. The hardness increased 1.18 times and the wear rate lower more than 50.5%. It also have a highly improvement to compare with the samples treated by convential nitriding, the result as shown in Table 3.

<table>
<thead>
<tr>
<th>Sample status</th>
<th>Laser nitriding</th>
<th>Conventional nitriding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness/HV</td>
<td>976</td>
<td>857</td>
</tr>
<tr>
<td>Wear rate/$\times 10^{-5}$mm$^3$/m$^\circ$N</td>
<td>1.59</td>
<td>1.88</td>
</tr>
</tbody>
</table>

The depth of hardened layer curve (as shown in Fig.3) indicated that the depth of hardened layer is 150$\mu$m, the maximum hardness at the top hardened layer, at 10$\mu$m below the surface hardness value will reach HV920. Through preliminary analysis, we considered that in laser processing the reactive [N] atom decomposed by NH$_3$ under the short time effect of laser has rapid cooling(about $10^5$~$10^6^\circ$C/s), therefore, only formed 10$\mu$m thickness of high-nitrogen phased nitride layer in the surface layer of the sample. In the sub-surface the nitrogen concentration decreased as ladder shape. At the internal of the hardened layer, as the long-pulse radiation induced thermal effect and quenching produces martensitic transformation, it formed a very fine tempered martensite. The hardened layer depth is about 150$\mu$m.

After laser nitriding, the SEM photos of sample (as shown in Fig.4) demonstrate that the surface of the nitrided layer appears dense and more regular stacking of multi-crystalline structure, simultaneously, exists obvious micro-cracks and a small amount of micro-porous. We think that micro-cracks and micro-porous is caused by stress release when the surface layer rapid melting and condensation at the process of pulsed laser nitriding.

Microstructure of sample cross-section analysis demonstrated that (as shown in Fig.5): modified layer mainly shows the structure of dendritic crystal, as the flow temperature field inside the melting pool is different caused by...
laser heating, so it has different cooling speeds in different parts of the melting pool. Initially, formatted nuclei has inconsistent growth rate in all directions, due to the faster scattering at the edges and corners so the growth rate is also faster, firstly, it forms the trunk, then grows branches, gradually, it forms dendritic structure. Dendritic crystal as the main structure of modified layer is the main factor for wear rate increase[7].

Blew the dendrite structure was composed by ultrafine martensite produced by laser hardening process, the crystal grain is small and dense. It has obvious refinement of martensite crystal through laser hardening process. In the rapid heating conditions ($10^5$~$10^6 ^{\circ}C/s$), significant of overheating degree cause the large phase transformation driving force ($\Delta G^{-\infty}$), it increase the number of crystal grain, simultaneously, for the sake of the rapid cooling after heating the ultrafine martensite too late to grow up.

![Fig.3 Laser nitriding hardening layer depth curve](image1.png)

![Fig.4 SEM photographs of Laser nitrided surface of sample](image2.png)

![Fig.5 SEM photographs of laser nitrided cross-section of sample](image3.png)
4. Laser Nitriding Process Analyses

Laser nitriding process as following:

Focused laser beam made GCr15 steel sample which placed in the NH₃ environment has formed metal melting pool on the surface; the energy of the laser beam is more concentrated, near the metal melting pool ammonia can decompose a lot of free activated N atoms (the atoms can purify the surface); substrate surface due to absorption of laser energy and in the molten state, the activated N atoms in melting pool will proliferate, and thus a large number of N atoms dissolved in austenite, in the subsequent acute cooling process, in which elements such as N atoms (or ions) and the Cr, Fe forms a high ε-phase Fe₂₋₃N solid solution, thereby enhancing the hardness of surface of the workpiece. On the one hand, under the influence of the laser can not only generate small uniform of the ε-phase Fe₂₋₃N solid solution, and the solid solution phase region extended further to the Ministry of the core samples. Moreover, along with the surface temperature rising at laser-treated zone, occurred phase-change reaction, transformed from austenite phase to martensite phase, it lead to phase transformation hardening. Thus, treated by laser can highly enhance hardness and depth of hardened layer. At the same time, metallurgical bonding exists between the nitrided layer and the substrate materials; due to the action characteristics of extremely hot or cold of pulsed laser, can get a more uniform composition and small grain cell to improve the hardness of the sample surface and the friction and wear properties. As the radius of N atom (RN) is 0.071nm, RN/RFe=0.071/0.126=0.57<0.59, therefore, with the nitrogen-treated steel GCr15 received nitride layer is Fe₂₋₃N-phase solid solution[9-11].

5. Conclusions

The use of pulsed laser in gas alloying method realized surfaces nitriding of GCr15 steel, formed large amounts of Fe₂₋₃N cubic phase of the hardening layer on the surface of the sample contains, the surface of hardened layer was dense and the comparison rules stacked multi-crystalline structure. The main structure of Hardened layer are dendrite, the grain is small and dense. Surface hardness of the nitrided layer reaches HV976.00, compared with the non-treated sample of which the hardness is HV447.97, its increased by 118%; hardened layer wear rate than before the treatments (3.21×10⁻⁵mm³/m•N) reduced to 1.59×10⁻⁵mm³/m•N, shows that resistance to grinding increase 51%; hardened layer depth is about 150μm. Compared with conventional nitriding treatment process, the laser nitriding process has a considerable increase (hardness increase 13.9% and wear rate decrease of 15.4%).

Inadequacy is due to laser rapid melting and subsequent quenching solidification stress release in the modified surface layer are easy to form micro-cracks and micro-porous, will affect the surface topography of workpiece, it needed follow-up further study.

References

4. HAO Shen-zhi,ZHONG Fu,DONG Chuang; “TECHNIQUE FOR SURFACE MODIFICATION OF MATERIALS BY HIGH-CURRENT PULSED ELECTRON BEAM”. Vacuum and Cryogenics, 2, P.77~80(2001).