Modification of high-chromium cast iron alloy by N and Ti ion implantation

L.R. Shen\textsuperscript{a,b}, K. Wang\textsuperscript{a}, J. Tie\textsuperscript{a}, H.H. Tong\textsuperscript{a}, Q.C. Chen\textsuperscript{a}, D.L. Tang\textsuperscript{a}, R.K.Y. Fu\textsuperscript{b}, P.K. Chu\textsuperscript{b,*}

\textsuperscript{a}Southwestern Institute of Physics, Chengdu, Sichuan, 610041, China
\textsuperscript{b}Department of Physics and materials Science, City University of Hong Kong, Tat Chee Avenue, Kowloon, Hong Kong

Available online 25 September 2004

Abstract

The effects of single- and dual-element (N and Ti) ion implantation on the properties of high-chromium cast iron alloys are investigated. Crystal defects, secondary hardening phase of CrN, and various crystal and amorphous forms are produced by ion implantation, and as a result, the microhardness, wear fatigue resistance, wear abrasion resistance, erosion resistance, and friction coefficient are improved. The developed technology has been successfully applied by the oil industry to prolong the lifetime of cylinder liners by three to four times and that of the rubber pistons in mud pumps by a factor of 2.

D 2004 Elsevier B.V. All rights reserved.

Keywords: Ion implantation; Surface modification; High-chromium cast iron liner

1. Introduction

Oil drilling machines used by oil companies have many components that are prone to damage under the adverse field conditions of high pressure, erosion, and harsh geological environment. Improving the lifetime of these components is one of the important tasks in the oil industry, and the research activities have focused on boronization, chromium coating, spray coating of hard-wearing alloy, and so on. Ion implantation is a widely accepted technique in the semiconductor industry but is only used sporadically in the metallurgical industry [1]. Some research works have been conducted to improve the mechanical and chemical characteristics of metals using ion implantation [2–5]. The influence of the implantation energy, implantation dose rate, current density of the ion beam on the phase, and the microstructure and properties of the low- and high-chromium steel have been studied [5–8]. Several elements, such as Cr, Ti, and N, can undergo different degrees of the phase formation and microstructural change, as well as mechanical and chemical enhancements. In the work reported here, single-/dual-element ion implantation is utilized to prolong the lifetime of cylinder liners in mud pumps made of high-chromium cast iron alloy. This component is one of the most susceptible parts to damages in oil drilling machines. Previously, oil pump materials and components modified by plasma immersion ion implantation in our laboratory exhibited improved chemical resistance [5]. This paper describes our recent experimental study with regard to the modification of the high-chromium cast iron alloy that is also often used in oil drilling machines by multiple ion implantation. Our latest results show that nitrogen or nitrogen plus titanium implantation can result in the formation of nitride phases in the near surface. Besides, the modified cylinder liners show significant improvement in terms of wear fatigue, wear abrasive, and erosion when they are subjected to the harsh conditions in field applications.

2. Experimental

High-chromium cast iron alloys with a composition of 2.8 wt.% C, 18 wt.% Cr, 0.3 wt.% Si, 0.7 wt.% Mn, and
the rest, iron, were studied. The specimens underwent the same industrial treatment as real parts in the oil pumps before they were cut, polished, cleaned, and dried for our investigation. Nitrogen and titanium ion implantation was carried out in a GLZ-100 industrial ion implanter, and the implantation conditions are displayed in Table 1. A rotating sample stage was used to ensure implant uniformity and reproducibility.

The microhardness of the unimplanted and implanted samples was measured with the Hx-1000A microhardness tester using a loading of 49 mN and time of 20 s. The wear fatigue test was carried out on a MM 200 dynamic load wear fatigue tester, and the wear abrasion test was performed employing a M-200 tester. The medium was water heated to 40–50 °C, together with some quartz sand, with a granularity of 0.1–0.2 mm, and the weight ratio of sand to water was 2:1. The friction coefficient was determined using a reciprocating tester; the medium was again water. The samples were analyzed using X-ray diffraction.

### 3. Results and discussion

The XRD results depicted in Fig. 1 show that N⁺ and (N⁺+Ti⁺) implantation processes produce a new CrN phase in the near-surface region. Compared with the unimplanted specimen, the Cr7C3 content increases, the Fe–C cementite

<table>
<thead>
<tr>
<th>Ion species</th>
<th>Ion energy (keV)</th>
<th>Dose (×10¹⁷ ions cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N⁺</td>
<td>75</td>
<td>4, 6, 8, 10</td>
</tr>
<tr>
<td>Ti⁺</td>
<td>35</td>
<td>2, 4</td>
</tr>
<tr>
<td>N⁺ and Ti⁺</td>
<td>75 and 35</td>
<td>6 and 2, 8 and 4</td>
</tr>
</tbody>
</table>

Table 1: Ion implantation conditions

![Fig. 1. X-ray diffraction of specimens implanted with various doses.](image1)

![Fig. 2. Relationship between nitrogen implant dose and microhardness.](image2)
content decreases by a factor of 2–3, and the α-Fe content increases by a factor of 1–2. In the Ti⁺-implanted sample, a portion of the Ti forms a solid solution, and the rest forms amorphous intermetallic compounds [9].

The impact of the nitrogen implant dose on the microhardness is shown in Fig. 2. In comparison with the unimplanted specimen, the microhardness increases with the implant dose at low doses. The maximum value of HV1350 that is about 2.5 times higher than that of the unimplanted sample is achieved at a dose of $8 \times 10^{17}$ ions cm$^{-2}$. When the implant dose exceeds this value, the hard phase begins to decrease. The increase in the hardness is believed to be due to the formation of new nitride phases in the modified layer. However, implantation with an excessive dose is not beneficial with regard to the hardness because the original hard phase (nitride phase) can be damaged to become an amorphous disordered phase.

Because the microhardness influences the wear abrasion of the specimen surface, the relationship between the resistance against wear abrasion and implant dose shown in Fig. 3 is similar to that of the microhardness. The weight loss is reduced with increasing nitrogen dose. The least weight loss is observed from the sample with an implant dose of $8 \times 10^{17}$ ions cm$^{-2}$ and is a quarter of that of the unimplanted specimen. Similar to the microhardness trend, the weight loss increases when the implantation dose exceeds this critical value. The wear fatigue versus implant dose relationship is exhibited in Fig. 4. The weight loss increases with the cycle number, and the weight loss of the specimen implanted with a dose of $6 \times 10^{17}$ ions cm$^{-2}$ is the least. Our results indicate that an excessively high implant dose gives rise to adverse effects, including more brittleness and mitigated wear fatigue, as well as wear abrading resistance.

Fig. 5 shows that the rate of change of the friction coefficient varies with the implant dose in both single- (N) and dual-element (N and Ti) implantation. The maximum decreasing rate of the friction coefficient is observed for the sample with an implant dose of $4 \times 10^{17}$ ions cm$^{-2}$. For this sample, the friction coefficient decreases by 28% compared with the unimplanted specimen. The decreasing rate of the dual-element-implanted specimen is higher than that of the single-element-implanted one. Our results show that the friction coefficient depends on both the nature of the implanted species as well as the implant dose.

4. Modification of cylinder liner in industrial oil pump by ion implantation

Mud pumps are used to transport highly pressurized caustic mud containing quartz sand. The typical working conditions are the following:

1. A rubber piston moves inside a cylindrical shell (liner) at 90–100 strokes/min, repeatedly. The pressure inside the liner is 10–20 MPa.
Ion implantation produces many types of crystal defects, secondary hardening phases of CrN, TiN dispersed in the near-surface region, amorphous components, and grain changes in the implanted layer. They increase the surface microhardness and reduce the friction coefficient. In addition, the implanted ions act as sinks stopping the diffusion of crystal defects and preventing dislocations and cracks from proliferating. Based on the common theory of wear [10], decreases in the friction coefficient and propagation speed of cracks increase the wear fatigue resistance of the modified liners effectively. If the surface microhardness $H_s$ of the surface is 1.3 times higher than the hardness $H_m$ of the abrading species, wear abrasion hardly takes place. Hence, it is reasonable that ion implantation reduces the wear abrasion of liners. The corrosion abrasion mechanism of liners is primarily electrochemical corrosion. The amorphous components in the implanted layer do not take part in electrochemical reactions. In addition, the radiation damaged and oxidized layer acts as a passivation layer, yielding smaller friction coefficient and lower propagation of structural cracks, and consequently, corrosion abrasion of the liner surface is mitigated. The ion implantation technique developed in this work not only shows good results in the laboratory but also increase the lifetime of high-chromium cast iron alloy liners in the field.

5. Conclusion

We have developed an experimental procedure to improve the surface properties of chromium cast iron alloy using single- and dual-element ion implantation and demonstrated the effectiveness on oil pump liners in the field. According to our findings, liners in the mud pumps experience tremendous wear abrasion, wear fatigue, and erosion, and wear fatigue plays an important role in the damage of the liners. Hence, reducing the friction coefficient is very important. Ion implantation produces crystal defects, secondary hardening phase of CrN, and various forms of crystalline and amorphous components to increase the microhardness, wear fatigue resistance, wear abrasion resistance, and erosion resistance and reduce the friction coefficient; and hence, ion implantation can prolong the lifetime of liners and rubber pistons. Our results obtained from drilling tests in an oil field are consistent with the results obtained from specimens tested in the laboratory. The lifetime of the modified liner is increased by three to four times, and that of the rubber piston is increased by a factor of 2. Our implantation technique enhances the durability and reliability of mud pumps, thereby promoting the production efficiency and reducing production cost.

Acknowledgements

This work was jointly and financially supported by the Hong Kong Research Grants Council (RGC) Competitive Earmarked Research Grant (CERG) No. CityU 1137/03E and the National Natural Science Foundation of China under Grant No.10275020.

References