Article

Numerical Simulation and Surface Properties of 42CrMo Steel Treated by Plasma Nitriding and Laser Quenching

Yuhang Zhang and Yixue Wang *

School of Materials Science and Engineering, Shanghai University of Engineering Science, Shanghai 201620, China
* Correspondence: sunnywang2013@sina.com; Tel.: +86-021-67791202

Abstract: In this study, we investigated the nitriding and laser quenching composite modified layers of 42CrMo steel. MATLAB was used to fit the nitrogen concentration distribution during nitriding, and the laser temperature field was fitted using ABAQUS finite element simulation software. Two groups of simulation results were integrated to fit the modified layer depth under different processes, and the nitriding and laser quenching experimental results were compared with the simulation results, which indicated that the simulation results agreed well with the experimental results. The depth of the nitriding–laser quenching composite layer greatly improved compared with the nitriding or laser hardening layers. The austenitizing temperature of the 42CrMo steel was reduced to 577 °C by nitriding. Therefore, the depth of the austenitized layer of the 42CrMo steel heated with the same laser power significantly increased. Under the same laser process conditions, more austenitic phase transformation was observed in the nitriding layer than in the non-nitriding layer, so martensitic phase transformation was more likely to occur in the subsequent cooling process. After plasma nitriding at 460 °C for 16 h and laser quenching, the modified layer depth of the 42CrMo steel reached 990 µm, and the average surface hardness of the 42CrMo steel reached 625 HV0.1. The friction coefficient of the modified layer was the lowest, with a value of 0.433, and the minimum wear value was 1.024 mm³. Double hardness and thickness of the modified layer could be obtained by nitriding and laser quenching composite processes.

Keywords: 42CrMo steel; numerical simulation; plasma nitriding; laser quenching; modified layer

1. Introduction

42CrMo steel is a high-strength medium carbon steel that is widely used in aviation, machinery, automobile, and other fields. This material has good corrosion resistance and fatigue resistance, but low cold deformation plasticity, poor weldability, and insufficient hardenability [1–3]. The service life of untreated 42CrMo steel will be reduced due to its low hardness and poor wear resistance. Under the service condition of long periodic high load, internal fatigue damage of the steel will easily occur, causing brittle fracture, which can lead to failure of the workpiece. Surface strengthening of materials is critical for increasing hardness, wear, and corrosion resistance, especially the load-bearing capacity and fatigue properties of machine components such as bearings and gears.

Various thermochemical treatments have been widely used to improve the surface properties of engineering steels, such as plasma nitriding [4–7], gas nitriding [8,9], plasma immersion ion implantation [10–14], and other surface modification methods, increasing the surface hardness, wear resistance, and corrosion resistance of steel or other iron-based alloys. Material fatigue damage often occurs beneath the surface, making it necessary to increase the depth and hardness of the modified layer to improve fatigue performance [15]. However, desired high-depth hardened layers obtained from nitriding will always be hindered by diffusion kinetics, which will approximately conform to parabolic law [16,17]. Genel [18,19] put forward an estimation method to predict the case depth of case-hardened steels and estimate their fatigue limit. A nitriding layer about 500 µm thick could be obtained by nitriding for several tens of hours, with sluggish growth kinetics. Microstructure
coarsening after extended nitriding at high temperatures will also deteriorate the load-bearing capacity and fatigue properties near the material surface. Therefore, increasing the thickness of the nitriding layer and reducing the brittleness of the nitriding layer may offer important technical significance for the engineering design of steel.

Laser quenching is an effective surface modification method with the advantages of fast speed, a narrow heat-affected area, and small shape variability [20–25]. This method has been employed in various industrial applications to improve the wear resistance and contact fatigue of steel components [26]. In the process of laser quenching, the surfaces of metal parts are rapidly heated to austenitic temperature range by laser heating, followed by rapid cooling to complete quenching, and finally the hardened martensite structure forms on the surface [27]. However, laser quenching treatment also has some shortcomings such as low toughness and poor wear resistance, with an inferior effect of laser quenching on microhardness compared with plasma nitriding. By combining the advantages of plasma nitriding and laser quenching, a modified layer with double hardness and thickness can be obtained to meet practical work requirements [28,29].

In this work, we used 42CrMo steel as an example material. The nitrogen concentration distribution field and laser quenching temperature field of the 42CrMo steel after nitriding and laser quenching were numerically simulated using MATLAB and ABAQUS finite element simulation software, and the modification layer depth under different technologies was predicted. The microstructure, phase composition, hardness distribution, and wear resistance of the composite modified layer after nitriding and laser quenching were investigated to verify the accuracy of the numerical simulations. Finally, the composite modification mechanism was revealed.

2. Materials and Methods

2.1. Materials

In this study, the program material was received as a 20-mm-diameter hot rolling bar of 42CrMo steel, with the chemical composition listed in Table 1. The 42CrMo steel was quenched at 850 °C, and then tempered at 560 °C (QT treatment). Planchet specimens with a thickness of 6 mm were cut from the bar and manually machined using silicon carbide paper using grades 240–800, to obtain an ideal surface condition. The specimens were thoroughly ultrasonically rinsed with deionized water, alcohol, and acetone before they were subjected to nitriding treatment.

Table 1. Chemical composition of quenched 42CrMo steel (wt.%).

<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>Cu</th>
<th>Mo</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.45</td>
<td>0.37</td>
<td>0.8</td>
<td>&lt;0.035</td>
<td>&lt;0.035</td>
<td>&lt;0.030</td>
<td>1.2</td>
<td>≤0.030</td>
<td>0.25</td>
<td>Balance</td>
</tr>
</tbody>
</table>

2.2. Plasma Nitriding

Plasma nitriding (PN) was carried out in a 50 kW LDMC-50F pulsed plasma nitriding furnace and conducted in a gas mixture of ammonia and methane with fixed flow rates of 1.0 and 0.1 L/min. The nitriding temperature was set at 460 °C, with nitriding times of 8 and 16 h. The specimens were then cooled down slowly to room temperature in a nitrogen atmosphere to avoid surface oxidation.

2.3. Laser Quenching

Laser quenching (LQ) was performed using a YLS-5000 CO₂ laser system with a nominal power of 5 kW operated under the following conditions: power \( p = 1 \) kW and scanning rate \( v = 10 \) mm/s. The untreated and nitriding surfaces were radiated with a continuous 5 mm wave CO₂ laser beam in air. The distance between the focusing mirror and the laser quenching surface was equal to 475 mm. This arrangement permitted high rates and low durations of the heating and self-quenching processes. The microhardness
and wear properties were compared between the nitriding–laser quenching (PN + LQ) and typical plasma nitriding processes.

2.4. Characterization

After treatment, the cross-sections were metallographically polished and etched with an alcohol solution containing 4% (vol.%) nitric acid, with the microstructures observed by a CMM-33E microscope. The section hardness was measured using an HV1000 micro-hardness tester under 0.1 kg of test force, and a CFT-I functional friction tester was used to measure the friction coefficients of the different process surfaces. Tungsten carbide with a diameter of 6 mm was used as the friction pair for circular motion, with an experimental load of 20 N, friction radius of 2 mm, and motor speed of 336 r/min. An MT-500 surface profiler was used for linear scanning in the direction of the vertical wear marks with a two-dimensional probe, and the wear value was measured three times at adjacent positions to obtain the average value per unit area.

To identify the different phase compositions of the specimens processed by QT, PN, LQ, and PN + LQ treatments, X-ray diffraction (XRD) analysis was carried out on the surface layers. A D/max-rB rotating anode X-ray diffractometer was used in this study, with Cu-K\(\alpha\) radiation (\(\lambda = 0.15405\) nm) in an incidence angle range of 20–100° at 40 kV and 30 mA.

2.5. Numerical Simulations

Plasma nitriding combines the diffusion of nitrogen, the precipitation of nitrides, and the formation of modified layers. The coupling of related processes makes it difficult to establish a nitriding model. Therefore, to optimize the calculation method and make use of the known thermodynamic data, some assumptions were made for the nitriding process. First, the diffusion of nitrogen in the solid solution was regarded as an equilibrium process in the nitriding process. Second, the effect of alloying elements on the nitrogen concentration distribution of the modified layer was considered negligible. Finally, in the nitriding model, the diffusion coefficient of nitrogen in each phase was not affected by the nitrogen concentration. Combined with the abovementioned assumptions, a one-dimensional plasma nitriding model was established.

2.5.1. Mathematical Model of Plasma Nitriding

In the process of nitriding, the mass transfer of nitrogen was expressed by Equation (1):

\[
\frac{\rho}{d} \frac{dN_s}{dt} = A - BN_s, \tag{1}
\]

where \(\rho\) is the density of the material, \(N_s\) is the surface nitrogen concentration, \(A\) is the constant determined by the forward reaction, and \(B\) is the constant determined by the reverse reaction. Because the forward reaction rate was much higher than the reverse reaction rate in the nitriding process [30], \(B\) could be approximated as 0. Equation (1) could be deformed as:

\[
\frac{dN_s}{dt} = \frac{A}{\rho} t \leq t_1 \tag{2}
\]

where \(t_1\) is the time to generate \(\gamma'\)-Fe\(_4\)N on the surface. Equation (2) represented the boundary conditions before the compound layer formed. In the plasma nitriding process, a concentration gradient distribution of the nitrogen atoms will form between the surface and the core, providing the driving force for the diffusion of nitrogen atoms in the matrix. The diffusion process was controlled by Fick’s second law:

\[
\frac{\partial N(x,t)}{\partial t} = \frac{\partial^2 N(x,t)}{\partial x^2}, \tag{3}
\]
where $N(x,t)$ is the nitrogen concentration at time $t$, with $x$ the distance from the surface, and $D$ is the diffusion coefficient of nitrogen in the $\alpha$ phase. At time $t < t_1$, Equation (3) would satisfy the second type of boundary conditions, according to:

$$-D \frac{\partial N(x,t)}{\partial x} \bigg|_{x=0} = \frac{\partial N_s}{\partial t} = \frac{A}{\rho},$$  

(4)

As the nitriding process continued, the surface nitrogen concentration reached the ultimate solubility of nitrogen in $\alpha$-Fe, and the nitrogen concentration remained unchanged during the subsequent diffusion process. After $t_1$, the boundary conditions changed to:

$$N(x = 0, t \geq t_1) = N_{\alpha/r},$$  

(5)

where $N_{\alpha/r}$ is the limiting solubility of nitrogen in $\alpha$-Fe.

The nitriding sample was assumed to be a half infinite body, and the second boundary condition was that the nitrogen concentration was a constant value at an infinite depth. At this time, the nitriding condition on both sides of the sample was the same, and the nitrogen flux at distance $h$ from the sample surface was 0; therefore,

$$\frac{\partial N(x,t)}{\partial x} \bigg|_{x=h} = 0,$$  

(6)

Before nitriding, the initial nitrogen concentration $N_0$ was 0, and the initial condition was:

$$N(x,t = 0) = 0,$$  

(7)

The nitriding process consisted of a reaction diffusion process, and the surface nitrogen concentration of the sample increased with prolonged nitriding time. After $t_1$ time, the saturation solubility of the $\alpha$ phase was reached, and $\gamma'$-Fe$_4$N compounds formed. The boundary condition between the compound layer and the diffusion layer was the boundary condition at this moment, and the critical condition of compound formation could be expressed by:

$$N(x = 0, t = t_1) = N_{\alpha/r},$$  

(8)

Together, Equations (3), (5) and (8) formed the mathematical model of plasma nitriding.

Because of the strong binding force between chromium and nitrogen in the 42CrMo steel, the formation of alloy nitride had to be considered in the nitriding process. These alloying elements with strong binding to nitrogen would preferentially react with nitrogen until the alloying elements were exhausted. We let $N(x,t)$ be the concentration of nitrogen and $M(x,t)$ be the concentration of alloying element at position $x$ distance from the sample surface at time $t$, and the form of nitride formed by it expressed as $MN$; thus, the reaction process could be expressed as:

$$N(x,t) + M(x,t) = MN,$$  

(9)

When the alloy nitride precipitated, the equilibrium solubility of the alloy nitride $K_{MN}$ should be less than the product of the equilibrium concentration of the nitrogen element and the concentration of the alloy element; therefore:

$$N(x,t)M(x,t) > K_{MN},$$  

(10)

After all the alloy nitrides with strong bonding effects to nitrogen precipitated, the other alloy nitrides that formed with slightly weaker nitrogen bonding forces started to precipitate, and the remaining nitrogen element concentration followed:

$$N_w = N_t - N_s = N_t - \frac{N_t + M_s}{p} - \sqrt{(N_t + M_s)^2 - 4 \frac{N_t M_s - K_{MN}}{p}},$$  

(11)
where \( N_e \) is the equilibrium solubility of the alloying nitriding, \( N_t \) is the total nitrogen concentration in the matrix, \( N_s \) is the nitrogen concentration of alloying nitriding formed by alloying elements with a strong binding force to nitrogen, \( M_s \) is the concentration of alloying elements with a strong binding force to nitrogen, and \( \beta \) is the atomic mass ratio of alloying elements to nitrogen. According to the literature [31], the equilibrium concentration of CrN can be expressed as:

\[
K_{\text{CrN}} = [\text{Cr}] [N] = 6.75 \times 10^2 \exp \left( \frac{-126847.9 \pm 27209}{RT} \right),
\]

(12)

2.5.2. Mathematical Model of Laser Quenching

The simulation of the laser quenching temperature field was calculated by the nonlinear transient heat conduction equation [32]:

\[
\rho C_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial x} \left( \lambda_x \frac{\partial T}{\partial x} \right) + \frac{\partial}{\partial y} \left( \lambda_y \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( \lambda_z \frac{\partial T}{\partial z} \right) + q_r + q_L,
\]

(13)

where \( \rho \) is the material density, \( C \) is the specific heat capacity of the material, \( T \) is the temperature, \( t \) is time, \( \lambda_x, \lambda_y, \) and \( \lambda_z \) refer to the thermal conductivity of the material in the \( x, y, z \) directions, respectively, and \( q_r \) and \( q_L \) refer to the laser irradiation energy and latent heat of phase transition, respectively. The surface heat source with Gaussian distribution was selected for laser quenching, with its power density distribution on the XOY plane given by:

\[
q(r) = q_{\text{max}} \exp \left( -3 \frac{r^2}{R^2} \right),
\]

(14)

\[
q_{\text{max}} = \frac{3Q}{\pi R^2},
\]

(15)

\[
r^2 = (x - vt - \chi_0)^2 + (y - y_0)^2,
\]

(16)

The Neumann boundary condition was selected as the thermodynamic boundary condition in the laser quenching process, and the specific contents included radiation acting on all the surfaces of the sample. The heat exchange mode of the bottom surface of the sample was heat conduction. The other surfaces were convection heat transfer in addition to the bottom:

\[
q' = - \left( \lambda_x \frac{\partial T}{\partial x} + \lambda_y \frac{\partial T}{\partial y} + \lambda_z \frac{\partial T}{\partial z} \right) = h(T - T_{\infty}),
\]

(17)

where \( q' \) is heat flux, \( h \) is heat transfer coefficient, \( T \) is the surface temperature of the material, and \( T_{\infty} \) is the ambient temperature. The convective heat transfer coefficient between the sample and the air was set at 30 W·m\(^{-2}\)·C\(^{-1}\), and the radiation coefficient of the sample was 0.35.

3. Results and Discussion

3.1. Simulation Results

3.1.1. Simulation Results of Plasma Nitriding

MATLAB software was used to simulate the nitrogen concentration distributions of the different nitriding processes. The simulation algorithm logic is shown in Figure 1. The distribution of nitrogen concentration at 8 and 16 h is shown in Figure 2. Compared with the 8 h nitriding sample, the surface nitrogen concentration of the 16 h nitriding sample was slightly higher, and the gradient of nitrogen concentration was smoother. The depth of the nitriding layer was about 500 \( \mu \)m after 16 h of nitriding, which was also higher than after 8 h of nitriding.
Before martensitic transformation, the sample completed the austenitization transition. With N as the austenitizing stable element, the diffusion of nitrogen atoms reduced the austenite transition temperature, which allowed austenite transition to occur more easily in the laser quenching process, along with martensite transformation in the subsequent cooling.
process. Compared with the nitriding sample, the laser quenching sample after nitriding contained more martensite transformation areas and had a better quenching effect.

The surface carbon content was assumed as 0.4 wt%. Based on the Fe–C–N ternary phase diagram, the \( A_{C1} \) temperature was regarded as the austenite transition temperature, and regression treatment was performed on the \( A_{C1} \) temperature to obtain the relationship between the nitrogen concentration and temperature change:

\[
T = -7923N^2 - 782.5N + 725.18, \quad N < 0.09481 ,
\]

\[
T = 577, \quad N > 0.09481 ,
\]

By converting the experimental data in Figure 2 into Equations (18) and (19), the \( A_{C1} \) temperature curves of the 42CrMo steel under different nitriding processes could be obtained, as shown in Figure 3.

![Figure 3. Curves of the \( A_{C1} \) temperature changes with depth under different nitriding times.](image)

According to the Fe–C binary phase diagram, when the mass percentage of carbon content was between 0.4 and 0.45 wt\%, the temperature of \( A_{C1} \) was 727 °C. In the Fe–C–N ternary phase diagram, the temperature of \( A_{C1} \) was 577 °C. This was well illustrated by the simulation results of the temperature variations in Figure 3, where the presence of the N element caused the \( A_{C1} \) temperature to drop. With increasing nitriding depth, the N concentration decreased, and the \( A_{C1} \) temperature increased from 577 °C to 727 °C.

### 3.1.2. Simulation Results of Laser Quenching

ABAQUS Finite element simulation software was used to establish a rectangular three-dimensional model, and the material attributes were defined by the input material density, Young’s modulus, Poisson’s ratio, thermal conductivity, and specific heat capacity, as shown in Table 2. After creating the section attribute, we entered the analysis step, where the convective heat transfer and radiation heat transfer values were set. The mesh module contained 30,000 meshes, and then the analysis job was submitted. We inserted the heat source load into the subroutine, where the input laser power was 1000 W, the scanning rate was 10 mm/s, and the spot area was 9 mm\(^2\). The temperature field curve is shown in Figure 4, indicating that the temperature gradually decreased with increasing depth. With laser scanning, the surface temperature of the sample quickly reached the austenite transition temperature and then cooled quickly to complete surface quenching.
Table 2. Thermophysical properties [33].

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Young’s Modulus (GPa)</th>
<th>Yield Stress (MPa)</th>
<th>Coefficient of Thermal Expansion (10^6/°C)</th>
<th>Thermal Conductivity (W/m²·°C)</th>
<th>Specific Heat (J/g·°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>213.89</td>
<td>956</td>
<td>10.6</td>
<td>0.044</td>
<td>0.46</td>
</tr>
<tr>
<td>50</td>
<td>212.73</td>
<td>922</td>
<td>10.6</td>
<td>0.044</td>
<td>0.47</td>
</tr>
<tr>
<td>100</td>
<td>210.26</td>
<td>841</td>
<td>10.6</td>
<td>0.044</td>
<td>0.49</td>
</tr>
<tr>
<td>150</td>
<td>207.43</td>
<td>786</td>
<td>10.7</td>
<td>0.044</td>
<td>0.51</td>
</tr>
<tr>
<td>200</td>
<td>204.17</td>
<td>746</td>
<td>11.2</td>
<td>0.043</td>
<td>0.52</td>
</tr>
<tr>
<td>250</td>
<td>200.45</td>
<td>716</td>
<td>12.6</td>
<td>0.042</td>
<td>0.54</td>
</tr>
<tr>
<td>300</td>
<td>196.24</td>
<td>692</td>
<td>16.7</td>
<td>0.041</td>
<td>0.57</td>
</tr>
<tr>
<td>350</td>
<td>191.57</td>
<td>674</td>
<td>21.8</td>
<td>0.040</td>
<td>0.59</td>
</tr>
<tr>
<td>400</td>
<td>186.46</td>
<td>658</td>
<td>21.8</td>
<td>0.039</td>
<td>0.62</td>
</tr>
<tr>
<td>450</td>
<td>180.93</td>
<td>645</td>
<td>21.7</td>
<td>0.037</td>
<td>0.65</td>
</tr>
<tr>
<td>500</td>
<td>175.02</td>
<td>635</td>
<td>21.7</td>
<td>0.036</td>
<td>0.68</td>
</tr>
<tr>
<td>550</td>
<td>168.77</td>
<td>460</td>
<td>21.6</td>
<td>0.035</td>
<td>0.73</td>
</tr>
<tr>
<td>600</td>
<td>162.20</td>
<td>417</td>
<td>21.5</td>
<td>0.034</td>
<td>0.80</td>
</tr>
<tr>
<td>650</td>
<td>155.37</td>
<td>215</td>
<td>21.4</td>
<td>0.032</td>
<td>0.87</td>
</tr>
<tr>
<td>700</td>
<td>148.15</td>
<td>130</td>
<td>21.1</td>
<td>0.031</td>
<td>0.97</td>
</tr>
<tr>
<td>750</td>
<td>133.09</td>
<td>87</td>
<td>20.8</td>
<td>0.030</td>
<td>0.89</td>
</tr>
<tr>
<td>800</td>
<td>128.62</td>
<td>66</td>
<td>20.2</td>
<td>0.027</td>
<td>0.60</td>
</tr>
<tr>
<td>850</td>
<td>124.32</td>
<td>56</td>
<td>19.6</td>
<td>0.026</td>
<td>0.38</td>
</tr>
</tbody>
</table>

The above thermophysical properties are reproduced from cited reference [33].

Figure 4. The variation curve of laser quenching temperature with distance from surface.

3.1.3. Prediction of Composite Modified Layer Depth

The hardening depth simulation results of the composite modified layer are shown in Figure 5, which were obtained by fitting the laser quenching temperature curve to the Ac₁ temperature variation curve with the layer depth. The intersection of the laser quenching temperature curve and the Ac₁ temperature curve for different nitriding times could be regarded as the deepest distance at which austenite transformation occurred. The temperature of Ac₁ decreased due to the diffusion of N during nitriding, whereas the nitriding time increased, the temperature of Ac₁ decreased further as the amount of nitriding increased. Under the same laser scanning power and speed, the austenitizing region of the sample after 16 h of nitriding was larger than that after 8 h of nitriding, so the depth of the composite modified layer also increased.
The simulated depths of the modified layers under different composite processes are shown in Table 3. The depth of the simulated modified layer after 16 h of nitriding and laser quenching was the deepest, at about 900 µm.

Table 3. Simulation results of the composite modified layer thickness under different process conditions.

<table>
<thead>
<tr>
<th>Composite Process</th>
<th>Modified Layer Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LQ</td>
<td>715</td>
</tr>
<tr>
<td>460 °C PN8h + LQ</td>
<td>789</td>
</tr>
<tr>
<td>460 °C PN16h + LQ</td>
<td>900</td>
</tr>
</tbody>
</table>

3.2. Experimental Results
3.2.1. Microstructure of the Composite Modified Layer

Figure 6a,b show the modified layer microstructures of the 42CrMo steel under different processes at 460 °C. The samples showed a bright white layer after 8 and 16 h of nitriding. The thickness of the white bright layer after nitriding for 8 h is about 5 µm, while the thickness of the white bright layer after nitriding for 16 h is about 7 µm. After 16 h of nitriding, the modified layer had a more obvious acicular structure, and the results indicated that more nitride precipitated after 16 h of nitriding. Figure 6c,d show the microstructures of the 42CrMo steel after laser quenching at 460 °C for different nitriding times. The thickness of the modified layer was further increased by laser quenching after nitriding. Compared with Figure 6c,d, the sample processed by laser quenching after 16 h of nitriding had a deeper modified layer. The compound modified layer showed a clear crescent shape distribution and no nitriding layer was observed, indicating that a large amount of Fe oxide (Fe₃O₄, Fe₂O₃) was generated after laser quenching. The decomposition of nitride resulted in the formation of a large amount of nitrogen-containing quenching martensite in the modified layer.
Figure 6. The microstructures of the modified layers in 42CrMo steel: (a) 460 °C PN8h, (b) 460 °C PN16 h, (c) 460 °C PN8h + LQ, and (d) 460 °C PN16h + LQ.

Figure 7 shows the XRD patterns of the 42CrMo steel modified layers with different processes. As shown in Figure 7a, the XRD diffraction peak of the sample treated with QT was an $\alpha'$-Fe single phase structure. After 8 and 16 h of nitriding, the diffraction peaks of the $\varepsilon$-Fe$_2$3N and $\gamma'$-Fe$_4$N nitride phases were observed. This revealed that nitride was formed after nitriding treatment. As shown in Figure 7b, after laser quenching, quenched martensite phase ($\alpha'$-Fe), nitride phases ($\varepsilon$-Fe$_2$3N and $\gamma'$-Fe$_4$N), and iron oxide phases ($\text{Fe}_3\text{O}_4$, FeO, and Fe$_2$O$_3$) were produced. The peak values of the $\varepsilon$-Fe$_2$3N and $\gamma'$-Fe$_4$N phases decreased after laser quenching, indicating that the decomposition of nitride occurred after laser quenching.

Figure 7. XRD contrast of the 42CrMo steel modified by different processes: (a) comparison between the original state and the nitriding process, and (b) comparison between the laser and composite processes.

3.2.2. Properties of the Composite Modified Layer

Figure 8 shows the microhardness curves of the 42CrMo steel nitriding and laser quenching composite modified layers. After 8 h of nitriding, the surface hardness of the sample reached 737 HV$_{0.1}$, while after 16 h of nitriding, the surface hardness of the sample reached 845 HV$_{0.1}$. The increase in hardness indicated that a large amount of nitride was
produced. Moreover, with extended nitriding time, more high-hardness nitriding phases precipitated. The depth of the modified layer increased greatly after laser quenching, and the average hardness was about 500 HV$_{0.1}$. Laser quenching after nitriding further increased the average hardness by about 100 HV$_{0.1}$, and the depth of the modified layer also improved. An increase of 50 HV$_{0.1}$ core hardness is considered the critical hardness of the modified layer. The critical hardness of the modified layer was considered 300 HV$_{0.1}$, and the depth corresponding to the intersection of the hardness curve was the depth of the modified layer at this time. Figure 8a shows that the thicknesses of the modified layer following the LQ and 460 °C PN8h + LQ processes were 710 and 875 µm, respectively, and the thickness increased by about 23%. Figure 8b shows that the thicknesses of the modified layers following the LQ and 460 °C PN16h + LQ processes were 710 and 990 µm, respectively, and the thickness increased by about 39%.

![Figure 8. Microhardness curves of the 42CrMo steel modified by plasma nitriding and laser quenching: (a) 460 °C PN8h, and (b) 460 °C PN16h.](image)

We found that single nitriding treatment and single laser quenching treatment could improve the surface hardness and thickness of the modified layers to a certain extent. However, after the nitriding and laser quenching composite processes, the hardness and thickness values of the modified layer of the matrix greatly improved, and modified tissue with excellent properties was obtained. The thickness of the modified layers under different processes is shown in Table 4.

<table>
<thead>
<tr>
<th>Composite Process</th>
<th>Modified Layer Thickness (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>460 °C PN8h</td>
<td>220</td>
</tr>
<tr>
<td>460 °C PN16h</td>
<td>230</td>
</tr>
<tr>
<td>LQ</td>
<td>710</td>
</tr>
<tr>
<td>460 °C PN8h + LQ</td>
<td>875</td>
</tr>
<tr>
<td>460 °C PN16h + LQ</td>
<td>990</td>
</tr>
</tbody>
</table>

Figure 9 shows the friction coefficient curves of the different modified layers under dry friction under a load of 20 N. The friction coefficient of the laser-treated surface changed relatively smoothly in approximately the first 7 min. After laser quenching, Fe$_3$O$_4$ generated on the surface played a certain lubricating role in the friction process. With an increase in friction time, the Fe$_3$O$_4$ content decreased, and the average friction coefficient increased and remained stable.
Figure 9. Contrast diagram of the friction coefficient of 42CrMo steel under different processes: (a) 460 °C PN8h compared with 460 °C PN8h + LQ, and (b) 460 °C PN16h compared with 460 °C PN16h + LQ.

Figure 9a shows that the friction coefficient finally stabilized at 0.674 after 8 h of nitriding, and the wear resistance was poor. Figure 9b shows that the friction coefficient finally stabilized at 0.469 after 16 h of nitriding, and the decrease in friction factor indicated a larger amount of γ′-Fe₄N wear-resisting phases in the permeating layer. The wear resistance of the nitriding samples after laser quenching further increased, where the friction coefficient of the PN16h + LQ following composite modification was the lowest, and the average friction coefficient was about 0.433.

Figure 10 shows the abrasion contour of the different modified layers. After 8 h of nitriding, the wear marks were the widest and deepest. By contrast, the narrowest and shallowest wear marks appeared on the samples after 16 h of nitriding and laser quenching. Table 5 shows the comparison of wear rates of the different processes, indicating minimum surface wear of the samples with the 460 °C PN16h + LQ process, with an area of 1.024 mm³. Plasma nitriding for 16 h significantly decreased the wear rate compared to the increase in wear resistance laser quenching contributed.

Figure 10. Abrasion contour of the 42CrMo steel samples treated with different processes.

Table 5. Wear volume of 42CrMo steel modified by different processes.

<table>
<thead>
<tr>
<th>Composite Process</th>
<th>Amount of Wear (mm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>460 °C PN8h</td>
<td>3.655</td>
</tr>
<tr>
<td>460 °C PN16h</td>
<td>1.317</td>
</tr>
<tr>
<td>460 °C PN8h + LQ</td>
<td>3.043</td>
</tr>
<tr>
<td>460 °C PN16h + LQ</td>
<td>1.024</td>
</tr>
</tbody>
</table>

The above data show that the composite modification technology could reduce wear rate, as well as improve the wear resistance.
3.2.3. Modification Mechanism of the Composite Process

The 42CrMo steel was modified by plasma nitriding and laser quenching. The results showed that the thickness of the modified layer significantly deepened and the surface hardness of the workpiece significantly improved.

According to the simulation results, the diffusion of nitrogen atoms reduced the eutectoid temperature of the surface layer from 727 °C to 577 °C. The diffusion depth of nitrogen increased and the region of austenitic transformation expanded with extended nitriding time. Under the same laser process conditions, austenitic phase transformation occurred more in the nitriding layer than in the non-nitriding layer, so martensitic phase transformation was more likely to occur in the subsequent cooling process. Therefore, the modified layer with double hardness and thickness could be obtained by the plasma nitriding and laser quenching composite process. Table 6 shows the comparison between the simulation results and the experimental results of the modified layer depth of the 42CrMo steel under different processes. We found that the numerical simulation results were basically consistent with the experimental results, and the prediction of the modified layer depth was realized.

Table 6. Comparison of the experimental and simulated values of the composite modified layer depth.

<table>
<thead>
<tr>
<th>Composite Process</th>
<th>Simulated Results (μm)</th>
<th>Experimental Results (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LQ</td>
<td>715</td>
<td>710</td>
</tr>
<tr>
<td>460 °C PN8h + LQ</td>
<td>789</td>
<td>875</td>
</tr>
<tr>
<td>460 °C PN16h + LQ</td>
<td>900</td>
<td>990</td>
</tr>
</tbody>
</table>

4. Conclusions

The mathematical model of 42CrMo steel was established and its surface properties were measured under different process conditions. Based on the simulation and experimental results, the following conclusions were drawn from this research.

1. Compared with the single plasma nitriding layer or laser quenching layer, the 42CrMo steel modified layer after plasma nitriding and laser quenching had a higher hardness and deeper depth.
2. The simulation results were in good agreement with the experimental results. After plasma nitriding at 460 °C for 16 h and laser quenching, the modified layer depth of the 42CrMo steel reached 990 μm. The difference between the simulation results was within 10%.
3. After plasma nitriding at 460 °C for 16 h and laser quenching, the average surface hardness of the 42CrMo steel reached 625 HV0.1. The friction coefficient of the modified layer was the lowest, with a value of 0.433, and the minimum wear value was 1.024 mm³. Fe₃O₄ on the surface after laser quenching could play a certain lubricating role in the friction process.
4. The experimental results show that the modified layer depth is 220 μm after nitriding at 460 °C for 8 h, and the modified layer depth is increased to 875 μm after plasma nitriding at 460 °C for 8 h and laser quenching. Similarly, the modified layer depth of 460 °C nitriding for 16 h is 230 μm, and the modified layer depth of plasma nitriding at 460 °C for 16 h and laser quenching is increased to 990 μm. The depth of the modified layer is significantly improved.

Author Contributions: Conceptualization, Y.Z. and Y.W.; investigation, Y.Z.; writing—original draft preparation, Y.Z.; visualization, Y.Z.; supervision, Y.W.; funding acquisition, Y.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Class III Peak Discipline of Shanghai-Materials Science and Engineering (High-Energy Beam Intelligent Processing and Green Manufacturing).
Data Availability Statement: Data available on request due to restrictions privacy. The data presented in this study are available on request from the corresponding author. The data are not publicly available due to the code flow used in numerical simulation belongs to the privacy of the research group.

Acknowledgments: We would like to thank Jiewen Wang, Xin Liu and Fuxin Wang for their help and contribution to the work of this paper. Thank you also to Lina Tang for her help and guidance to the author.

Conflicts of Interest: The authors declare no conflict of interest.

References

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.