Investigation on Nano-Self-Lubricant Coating Synthesized by Laser Cladding and Ion Sulfurization

Meiyan Li, Bin Han, Conghua Qi, Yong Wang, and Lixin Song

1 College of Electromechanical Engineering, China University of Petroleum, 66 Changjiang West Road, Qingdao 266580, China
2 Offshore Oil Engineering (Qingdao) Co., Ltd., Qingdao 266520, China

Correspondence should be addressed to Meiyan Li; limeiyan@upc.edu.cn

Received 5 January 2015; Accepted 13 March 2015

The composite processing between laser cladding and low temperature (300°C) ion sulfurization was applied to prepare wear resistant and self-lubricating coating. The microstructure, morphology, phase composition, valence states, and wear resistance of the composite coating were investigated by scanning electron microscopy (SEM), atomic force microscope (AFM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and friction and wear apparatus. The results indicate that the laser cladding Ni-based coatings and the maximum hardness of 46.5 HRC were obtained when the percent of pure W powder was 10%, composed of columnar dendrites crystals and ultrafine dendritic structure. After ion sulfurization at 300°C for 4 h, the loose and porous composite coating is formed with nanograins and the granularity of all grains is less than 100 nm, which consists of γ-(Fe, Ni), M23C6 carbides, FeS, FeS2, and WS2. Furthermore, the wear resistance of the composite coating is better than the laser cladding Ni55 + 10% W coating, and the friction coefficient and mass losses under the conditions of dry and oil lubrication are lower than those of laser cladding Ni55 + 10% W coating.

1. Introduction

In order to improve the wear resistance of the key parts, in recent years advanced rapid solidification technologies such as laser surface processing [1–4], thermal spraying [5], and plasma spraying [6–8] have been reported to be feasible routes for enhancing the surface properties of the steel substrates. Among these surface techniques, laser cladding is considered to be one of the most promising due to the unique properties of wear resistance, metallurgical bonding, low dilution, and the increasing service life of metal parts. Zhan et al. have shown that the appearance of the high-power laser and the wideband scanning device offers a new effective method for the modification of material surface [9]. However, a hard surface will accelerate the wear of its counterpart, and it is ineffective for preventing the strain fatigue of the substrate, which will result in the failure of scuffing [9]. In this case, it is a good way to prepare the solid lubrication on the surface of wear resistance coating [10–12].

As we know, the sulfide FeS is a kind of effective solid lubrication with high melting point and can improve the self-lubricating property of materials obviously. Ion sulphurizing technology has been applied to prepare FeS film on the metal surface, which remarkably increased the self-lubricating property [10–12]. However, the studies of the coatings, with the properties of wear resistance and self-lubricating at the same time, prepared by laser cladding and low temperature ion sulfurization technology have not been reported in the literatures.

The goal of this work was to prepare the soft solid lubrication coating on the laser cladding Ni-based layer by means of low temperature ion sulfurization and to examine the microstructure, composition distribution, and properties.

2. Experimental Procedure

The samples of 45 steel were heat-treated by quenching and low temperature tempering and machined to the rectangular
Table 1: Chemical composition of 45 steels (wt, %).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.42–0.50</td>
<td>0.17–0.37</td>
<td>0.50–0.80</td>
<td>≤0.04</td>
<td>≤0.25</td>
<td>≤0.25</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 2: Chemical composition of Ni55 alloying powder (wt, %).

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Fe</th>
<th>Mn</th>
<th>Mo</th>
<th>Al</th>
<th>Si</th>
<th>B</th>
<th>S</th>
<th>P</th>
<th>Ni</th>
<th>Bal.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.66</td>
<td>16.28</td>
<td>25.63</td>
<td>0.15</td>
<td>0.01</td>
<td>2.92</td>
<td>2.21</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>53</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Table 3: Hardness of Ni55 + W laser cladding layer (HRC).

<table>
<thead>
<tr>
<th>Powders</th>
<th>Ni55 + 5%W</th>
<th>Ni55 + 10%W</th>
<th>Ni55 + 15%W</th>
<th>Ni55 + 20%W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness/HRC</td>
<td>44.7</td>
<td>46.5</td>
<td>39.3</td>
<td>35.8</td>
</tr>
</tbody>
</table>

Table 4: EDS results of the composite coating for different times (atom %).

<table>
<thead>
<tr>
<th>Elements</th>
<th>O</th>
<th>S</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
<th>W</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1h</td>
<td>15.59</td>
<td>2.48</td>
<td>9.41</td>
<td>34.49</td>
<td>9.42</td>
<td>5.90</td>
<td>22.71</td>
</tr>
<tr>
<td>3h</td>
<td>23.94</td>
<td>3.42</td>
<td>8.70</td>
<td>27.50</td>
<td>8.02</td>
<td>4.02</td>
<td>24.40</td>
</tr>
<tr>
<td>4h</td>
<td>19.95</td>
<td>3.56</td>
<td>6.98</td>
<td>24.74</td>
<td>11.56</td>
<td>3.37</td>
<td>29.84</td>
</tr>
</tbody>
</table>

shape of 45 mm × 45 mm × 10 mm as the substrate, and the chemical composition is listed in Table 1. The substrate is composed of ferrite and pearlite with the hardness of 150 HV0.1. The laser cladding Ni-based powder is mixed with Ni55 and different percents of pure W powders, and the chemical compositions of Ni55 powder are listed in Table 2. And the cladding powder is preplaced on the samples with the thickness of 1 mm. Laser cladding was performed using a continuous wave CO2 laser. A laser power of 3.5 kW at the work piece with a beam size of 10 mm × 1 mm and scanning velocity of 200 mm/min was applied. After laser cladding, the surfaces of specimens were polished with the surface roughness Ra of 0.8 μm and all specimens were simultaneously sulfurized in the furnace of low-temperature ion sulfurization (300 °C) for 1 h, 3 h, and 4 h, respectively.

X-ray diffraction (XRD) was utilized to analyze the phase structures of the laser cladding layer and sulfide composite coating. Atomic force microscope (AFM) and scanning electron microscope (SEM) equipped with EDS were employed to analyze the morphologies of surface and cross section of the sulfide composite coatings. EPMA scanning was carried out to study the distribution of elements within the composite coating. X-ray photoelectron spectroscopy (XPS) was used to detect the valence states of the sulfide composite coating.

The friction and wear tests were carried out on a ball-on-disc test rig of MMU-5G model. The upper sample was GCr13 steel ball with diameter 4 mm with the hardness of 60 HRC, and the lower samples were specimens treated by laser cladding and laser cladding-ion sulfurizing composite treatment with dimension of 43 mm × 5 mm. The wear tests were carried out under dry friction condition and the lubrication condition with number 40 machine oil (without any additives). The kinematic viscosity was 37–43 mm²/s at 50 °C and the velocity of oil supply was 2 mL/min. The load of 50 N and a velocity of 50 rpm for 60 min were chosen to test the variation of friction coefficient with time. The wear conditions were a normal load of 50 N, a sliding speed of 0.63 m/s, and the test time of 60 min.

3. Results and Discussion

3.1. Selection of Process Parameters. In this experiment, the weight percent of pure tungsten powder included in Ni55 alloy powder is 5%, 10%, 15%, and 20%, respectively. And the hardness values of the laser cladding Ni-based coatings are listed in Table 3. It can be seen that the hardness of the cladding coating reaches its maximum of 46.5 HRC at the percent of 10% W.

Figure 1 illustrates the morphologies of Ni55 + 10% W sulfide coatings at different sulfurizing times. It can be seen that the increase of sulfurizing time makes the surface of the composite coating darken.

The EDS analysis results of the composite coating with different sulfurizing times were shown in Table 4. The content of S element increases gradually with the increment of sulfurizing time, and highest value can reach 3.56% at the time of 4 h.

3.2. Microstructures of Laser Cladding Ni55 + 10% W Coating. For the range of parameters adopted in the experiments, a dense, uniform, and crack-free structure was obtained. Microstructural examination of the cladding Ni55 + 10% W coating shows that a thin layer of planar growth was present at all interfaces with an extension of around 3 μm–5 μm and a combination of columnar dendrites crystals and ultrafine dendritic structure (Figure 2).

The bottom and the middle region show cellular/dendritic structures (Figures 2(a) and 2(b)), while the upper region consists of ultrafine dendrites (Figure 2(c)). The solidification structure of the laser cladding layer mainly depends upon the solid-liquid interface growth rate R and the temperature gradient in the melt G. According to the numerical simulation of heat flow process in the molten pool [13], laser cladding is a rapid heating and rapid cooling process, and there exists an extremely high temperature gradient in the laser molten pool. Such variation in temperature results in the variation
in the ratio of temperature gradient ($G$) to the growth rate ($R$) during solidification following laser cladding. Thus, the $G/R$ value becomes the controlling factor for the morphology selection. As the $G/R$ ratio changes from its highest value at the bottom to its lowest one on the surface, such variation results in the variation in the degree of constitutional supercooling, leading to a complex solidification structure in the laser cladding coating.

According to the XRD analysis result in Figure 3, the laser cladding Ni55 + 10%W coating is composed of $\gamma$-(Fe, Ni), $M_{23}C_6$ and WC carbides.

3.3. Phase and Structural Analysis of the Ni55 + 10%W Sulfide Composite Coating. The phase and structural analysis of the Ni55 + 10%W sulfurized at 300°C for 4 h were analyzed. The XRD analysis result in Figure 4 indicates that the composite coating consists of $\gamma$-(Fe, Ni), $M_{23}C_6$ carbides, FeS, FeS$_2$, and WS$_2$.

Figure 4 illustrates the surface morphology of the Ni55 + 10%W sulfide composite coating observed under AFM. The 3D morphology in Figure 5(a) reveals the loose and porous characteristics of the composite coating, which is formed with nanoscale spherical grains. Moreover, the granularity of all grains is less than 100 nm.
EPMA scanning analysis results of the Ni55 + 10%W sulfide composite coating are shown in Figure 6. We can see that the contents of C, Fe, Ni, B, and Cr elements are high and these elements distribute uniformly. After laser cladding, these elements remain in solid solution in the austenitic matrix, playing a role of solid solution strengthening. Furthermore, the content of W element in the Ni55 + 10%W sulfide composite coating is high due to the additional introduction of pure W powder. Particularly, S element distributes unevenly resulting from the selective reaction with Fe element and W element, such as the formations of FeS, FeS₂, and WS₂.

Figure 7(a) is the cross-sectional morphology of the Ni55 + 10%W sulfide composite coating. It can be seen that the width of the sulfide composite coating is about 2 μm. According to the distribution of S element along depth direction, it is clear that no transition zone was found between the composite layer and the cladding layer (Figure 7(b)).

XPS analysis was introduced to study the chemical composition of the Ni55 + 10%W sulfide composite coating etched for different times, and the results were listed in Table 5 and the atomic percents were shown in Figure 8. We can see that with the etched time increase the content of S element increases and then decreases.

The valence states of Fe, S, and W in the Ni55 + 10%W sulfide composite coating etched for 300s were analyzed by XPS, as shown in Figure 9. It could be concluded that there were four phases present in the sulfide composite coating. One was dominant single substance Fe, and the other phases were solid lubricants FeS, WS₂, and FeS₂, which is consistent with the XRD result. Both FeS and FeS₂ were produced, but only FeS acts as the solid lubricant, because FeS₂ does not possess the close-packed hexagonal structure. Owing to more content of tungsten, the solid lubrication phase of WS₂ was also formed in sulfide layer of the Ni55 + 10%W cladding coating. As shown in Figure 9(a), the strong peaks of Fe appear near the binding energies 706.5 eV, 707 eV, and 709.7 eV, respectively. According to the standard pattern of electron binding energy of Fe element [14–16], the strong peak near 706.5 eV is corresponding to the Fe²⁺ in FeS₂ and the strong peak near 709.7 eV is assigned to the Fe²⁺ in FeS, while the strongest peak at 707 eV is contributed by the monoatomic Fe. In addition, the peaks near 161.5 eV and 161.7 eV shown in Figure 10(b) are corresponding to the S⁻² in FeS, the peaks at 162.1 eV are identified as the S⁻¹ in FeS₂, and the peaks near 162.4 eV and 162.9 eV are assigned to the S⁻¹ in WS₂. It means that, besides FeS and WS₂, a small quantity of fragile FeS₂ with nonlubricity is also formed on the surface of the laser cladding-ion sulfurizing composite coating due to the surplus S atoms on the surface.

3.4. Friction Coefficient and Mass Loss. Figure 9 shows the friction coefficients of the Ni55 + 10%W cladding coating and the Ni55 + 10%W sulfide composite coating under the conditions of dry and oil lubrication. As it can be seen, the sulfurized Ni55 + W coating possesses lower friction coefficient under the conditions of dry (Figure 10(a)) and oil (Figure 10(b)) lubrication, and the lower friction coefficient
Table 5: Chemical composition of Ni55 + 10%W sulfide composite coating etched for different times.

<table>
<thead>
<tr>
<th>Etched time/s</th>
<th>Cls</th>
<th>Ols</th>
<th>Fe2p</th>
<th>S2p</th>
<th>Cr2p</th>
<th>Ni2p</th>
<th>W4f</th>
<th>Si2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>65.6414</td>
<td>26.0216</td>
<td>2.65498</td>
<td>2.02515</td>
<td>0.472699</td>
<td>0.631961</td>
<td>0.403379</td>
<td>1.9669</td>
</tr>
<tr>
<td>1500</td>
<td>8.40491</td>
<td>3.5191</td>
<td>42.7755</td>
<td>2.36077</td>
<td>8.54908</td>
<td>18.1784</td>
<td>13.8193</td>
<td>2.2815</td>
</tr>
</tbody>
</table>

Figure 6: EMPA scanning analysis of Ni55 + 10%W sulfide coating. (a) B; (b) S; (c) Ni; (d) C; (e) Fe; (f) W; and (g) Cr.

for two coatings appears under oil lubrication. The friction coefficient of the Ni55 + 10%W cladding coating is about 0.9 and it reduced to 0.65 for the sulfide composite coating under dry condition. However, under the condition of oil lubrication, the friction coefficient of the Ni55 + 10%W sulfide composite coating is 0.075, which is reduced by 40% compared with the Ni55 + 10%W cladding coating. Particularly, the variation of friction coefficient of the Ni55 + 10%W sulfide composite coating was very smooth, indicating that under oil lubrication the composite coating was sliding at a quite steady state.

According to the results shown in Figure 11, the mass losses of the Ni55 + 10%W sulfide composite coating are much lower than those of laser cladding Ni55 + 10%W coating.
These results indicate that the Ni55 + 10%W sulfide composite coating reflects better wear resistance than the laser cladding coating, and it is feasible to improve the wear resistance of Ni-based cladding coating by ion sulfurization processing.

According to the tribological theory, an ideal friction surface should be soft at the surface, possessing excellent lubricating property, and hard at subsurface; that is, the hard substrate can give a sufficient support to the lubrication layer and keep a longer time of its effect. The hardness of sulfuration layer is very low, about 50–100 HV [17], while the hardness of the Ni55 + 10%W cladding coating is high, reaching 46.5 HRC, which is helpful for the improving of the wear resistance.

In addition, the Ni55 + 10%W sulfide composite coating is composed of γ-(Fe, Ni), M23C6 carbides, FeS, FeS2, and WS2, and the FeS and WS2 are the typical solid lubricant. As we know, similar to MoS2 and graphite, WS2 has close-packed hexagonal layered structure, and the lattice constants are a = 0.318 nm and c = 1.25 nm. Each tungsten atom connects two sulfur atoms and tungsten atom and sulfur atom are connected by strong chemical bond, while sulfur atoms are connected by weak molecule bond. According to the investigations in [18], the friction coefficient of WS2 is very low and it can protect metal surface from adhesion. Moreover, the crystal lattice of FeS is a close-packed hexagonal structure, and lattice constants are a = 0.597 nm and c = 1.174 nm. It can easily slip along close-packed plane, and the plastic rheology is good and the melting point is as high as 1100°C. When the friction-pair is sliding mutually, the partial FeS and WS2 films are adhered to the surface of steel ball and filled in its valley so that its surface is also covered with a solid lubrication film. The self-acting transfer of the solid lubricant between the friction-pair improves the lubrication condition [19]. So the Ni55 + 10%W sulfide composite coating can improve remarkably the properties of wear resistance and antifriction.

4. Conclusions

(1) Laser cladding was applied to prepare the Ni-based coatings and the maximum hardness of 46.5 HRC was obtained when the percent of pure W powder was 10%.

(2) The laser cladding Ni55 + 10%W coating is composed of a thin layer of planar growth and a combination of columnar dendrites crystals and ultrafine dendritic structure.

(3) After ion sulfurization, the loose and porous composite coating is formed with nanospherical grains and
Figure 9: XPS analysis of the Ni55 + 10%W sulfide composite coating. (a) Fe; (b) S; and (c) W.

Figure 10: Friction coefficient curves of different coatings: (a) dry friction; (b) oil lubrication.
the granularity of all grains is less than 100 nm. And the Ni55 + 10%W sulfide composite coating consists of γ-(Fe, Ni), M$_{23}$C$_6$ carbides, FeS, FeS$_2$, and WS$_2$.

(4) The Ni55 + 10%W sulfide composite coating reflects better wear resistance than the laser cladding coating, and the friction coefficient and mass losses under the conditions of dry and oil lubrication are lower than those of Ni55 + 10%W cladding coating.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors would like to acknowledge the supports from Open Fund (OGE201403-04) of Key Laboratory of Oil & Gas Equipment, Ministry of Education (Southwest Petroleum University), the National Natural Science Foundation of China (51179202), and the Natural Science Foundation of Shandong Province (ZR2014EEQ037).

References


