Influence of microstructure on the wear mechanism of multilayered Ni coating deposited by ultrasound-assisted electrodeposition

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Multilayered Ni coating, which is a laminated structure of (ordinary Ni layer)/(ultrasonic Ni layer), was obtained by ultrasound-assisted electrodeposition method on 18–8 stainless steel substrates. Its wear property compared with that of ordinary Ni coating. The crystallographic texture and surface morphology of the coatings were analyzed by means of XRD and SEM, respectively. The multilayered Ni coating exhibits higher wear resistance compared to that of the ordinary Ni coating. The wear mechanism of the multilayered Ni coating is the adhesive wear, which is a kind of the so-called micro-area detachment; while that of the ordinary Ni coating consists of the fatigue and adhesive wear due to its columnar microstructure.

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1. Introduction

Recent experimental researches on the wear behavior of nanosized coating materials have focused on dual-phase alloys and composites, and show that nanosized coating materials exhibit improved wear resistance compared with their coarse structured counterparts [1–5]. However, systematic studies of wear in pure nanocrystalline metals are less common. Nowadays, it is still a difficult task that the pure coatings overcome the drawbacks—pinholes [6,7], formed by columnar grains [8–11]. Under wear conditions, attempts have been made to improve the service life using lubricants [12,13] retarding in the columnar structure. During the wear service, in rough regions, the damage of plasma-sprayed ZrO$_2$ and Al$_2$O$_3$ coatings was a micro fracture along the columnar grain boundaries [14,15]. What’s more, detachment of the wear debris of TiAlCrYN and TiAlCrN by PVD method frequently occurred when cracks parallel to the worn surface intercepted a crack perpendicular to the worn surface usually along a columnar grain boundary which was opened up as a result of the bulk-fracturing action [16,17]. Therefore, the columnar grain is the chief culprit for the quick failure of the coatings. However, few investigators focused their concentrations on wear failure mechanism of electrodeposited pure Ni coatings. Jeong et al. [18] examined the effect of grain size on the wear of nanocrystalline nickel electrodeposits, which focused on grain sizes where the Hall–Petch strengthening relationship is valid. Other researchers studied the properties of metallic host material coatings modified with the addition of a second phase [19–21].

Recently, researchers found that ultrasonic introduction into electrodeposition can refine the grain sizes [22,23], which can enhance the hardness of the coating and the corrosion resistance. However, just as the electrodeposited coating in the continuous ultrasonic field is comparatively hard, its brittle tendency is greatly increasing with the thick coating thickness, so as to present a microcrack and even crack expansion.

Hence, we develop an ultrasound-assisted electrodeposition process through which the columnar grain mode of the coatings can be changed into the multilayered microstructure. This paper reports our work that multilayered Ni (M-Ni) coating was obtained by the ultrasound-assisted electrodeposition. During the experiment, we found that the ultrasonic frequency in the range of 5 kHz–15 kHz can only result in the grain refinement without other benefits, as the morphologies of their cross sections are also columnar grains. However, when the ultrasonic frequency reaches beyond 22 kHz, the cross-sectional morphologies of the columnar grain annihilate in the SEM observations. Therefore, we studied the influence of the microstructure on wear mechanism between the multilayered Ni coatings and the ordinary Ni (O-Ni) coatings in this ultrasonic condition.

2. Experimental procedure

2.1. Preparation of the coatings

18–8 stainless steel (1Cr18Ni8) was used as the substrate. The substrates were sandpapered with waterproof abrasive paper to 2000-grit, whileafter ultrasonically cleaned for 5 min in acetone solution. For surface activation, the substrates were immersed in acid solution (H$_2$SO$_4$: 230 ml/l, HCl: 70 ml/l, HNO$_3$: 40 ml/l) for about 3 min. Then, the substrates were washed with deionized water before the electrodeposition
of Ni coatings. The substrate was used as cathode, and two Ni plates were used as anodes located vertically on both sides of the cathode. The composition of the nickel electrodeposition solution and the depositing parameters are listed in Table 1.

The schematic diagram of the ultrasound-assisted electrodeposition device is shown in Fig. 1. The depositing bath was placed in the ultrasonic cell. The Ni coating was prepared without any ultrasonic agitations, namely O-Ni coating.

The process of the M-Ni coatings is as follows:

1. During the deposition of the M-Ni coatings, the mode of ultrasonic introduction is that the ultrasonic wave was introduced for 60 s at 60-second intervals in this experiment repeatedly;
2. The power and frequency of ultrasound are 600 W and 25 kHz, respectively.

In this way, the M-Ni coating is stacked by the modified Ni layer with ultrasound and the ordinary Ni layer without ultrasound repeatedly. Moreover, it needs to be ensured that both the top layer and the bottom layer adjacent to the substrate are the ultrasonic ones.

In order to compare the characteristics of the ultrasonic layer and the ordinary layer, a bilayered Ni (B-Ni) coating on 18–8 stainless steel was also prepared with a two-step deposition process as follows: in the same electrodeposition condition, the ultrasonic Ni (U-Ni) layer was firstly deposited for 30 min with ultrasonic agitation, and then the O-Ni layer was deposited for 30 min without ultrasonic agitation.

### Table 1
Composition of the depositing solution and the depositing parameters.

<table>
<thead>
<tr>
<th>Component</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄·6H₂O</td>
<td>250 g/l</td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td>40 g/l</td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>35 g/l</td>
</tr>
<tr>
<td>Sodium laurel sulfate</td>
<td>0.05 g/l</td>
</tr>
<tr>
<td>pH</td>
<td>3.8–4.5</td>
</tr>
<tr>
<td>Temperature</td>
<td>45–55 °C</td>
</tr>
<tr>
<td>Current density</td>
<td>0.6 A/dm²</td>
</tr>
<tr>
<td>Anode</td>
<td>Ni (purity: 99.96%)</td>
</tr>
<tr>
<td>Cathode</td>
<td>18–8 stainless steel</td>
</tr>
</tbody>
</table>

2.2. Characteristics of the coatings

Cross sections in thickness of about 20 μm were prepared by cutting the coating samples vertically to the surface, then grinding them and polishing them mechanically. Afterwards, cross sections were etched by a solution of 5 g FeCl₃, 15 ml HCl and 60 ml alcohol for about 20 s. Cross section morphologies of both the M-Ni coating and the B-Ni coating were observed by a scanning electron microscope (SEM) (XL-30FEG). X-ray diffraction (XRD) patterns of the samples were collected on an X'Pert-PRO diffractometer (PANalytical), using Cu Kα radiation with an accelerating voltage of 40 kV and a generator current of 40 mA, to analyze the texture of the Ni coatings. Moreover, the average grain size was calculated from XRD analysis (by the X’Pert HighScore Plus) in terms of diffraction line broadening of seven single Bragg reflection peaks (by the Wilson method) [24].

2.3. Microhardness

Microhardness of the M-Ni and O-Ni coatings was measured under a load of 0.49 N for 15 s with a Vickers hardness tester (Shimadzu Type-M). The coating thickness in this part should be taken into account. Three points were measured on each sample, averaging the values as the microhardness of the Ni coatings.

2.4. Adhesion assessment

Adhesion performance of the M-Ni and O-Ni coatings to the substrate was evaluated by bidirectional bend method, shown in Fig. 2. Sheets of 18–8 stainless steel of 0.12 mm thickness are employed as the substrates. A detailed description can be found in previous work [25]. Coating thickness for both Ni coatings is taken into consideration. The critical cycle number of the sample was selected as the criterion for describing the adhesive performance of the coating to the substrate the moment the coating under strain began to detach from the substrate.

2.5. Evaluation of wear resistance

Wear resistance of the M-Ni and O-Ni coatings was assessed with a NUS-LSO-1 type rubber wheel tester. The sample dimensions were 40×20×2 mm³, coated with the thickness of 20 μm. The test conditions were 400-grade emery paper and 6.3-N load. Before the wear test, the surface of the coated samples was carefully cleaned using acetone. Mass loss of the samples was measured with a FA1104N analytical balance (Minqiao). The samples were carefully cleaned and dried before the measurement of mass loss. After a 600-number-cycle and 1500-number-cycle, cross sections of the worn Ni coating samples along the wear direction were observed by means of SEM respectively.
Moreover, the worn surface tracks of both Ni coatings were also inspected after the 3000-number-cycle.

3. Results and discussion

3.1. Morphology of Ni coatings

SEM image of the cross section of the M-Ni coating is shown in Fig. 3a. From Fig. 3a, it can be observed that it is clearly a multilayered microstructure of stackered-up sandwiches. Thereinto, the white layers are the modified Ni layers with ultrasonic agitation, and the dark ones are the O-Ni layers without ultrasonic agitation. The M-Ni coating was produced with the thickness of each layer in about 45 nm.

From Fig. 3b (arrowed lines), it can be evidently observed that the grains of the U-Ni layer grow preferentially in the manner parallel to the substrate surface, compared to the O-Ni layer, with columnar growth vertical to the substrate surface. It can be inferred that the grain growth orientation of the U-Ni layer was along the direction of ultrasonic agitation. The slight different color in the U-Ni layer is the boundary of this kind of Ni nano-crystalline, because their grain size is very small as reported in Section 3.2. It can be considered as textured that the ordinary layers are vertically situated by the electric field resulting in the formation of separated columnar growth, i.e. field oriented crystals at the most negative potential [26]. However, as seen in Fig. 1, the plane of the located sample surface is parallel to the direction of ultrasonic generation under the cell, so the modified layers are horizontal because of the ultrasonic introduction, which may play a guiding role in the grain growth.

3.2. XRD results

Fig. 4 shows the XRD diffractograms of both Ni coatings. For the M-Ni coating, the peak intensity of (111) orientation becomes strong, while the ones of (200) and (220) turn weak. The preferred (111) orientation can be attributed to the effect of the ultrasonic agitation which can largely affect the grain texture of the Ni coating. In this study, when the ultrasonic waves spread in the medium, tens of thousands of small negative-pressure bubbles are produced and these bubbles with certain high pressure produce series of intensive explosions on the surface of the cathode, to enhance the surface activity of the cathode substrate and accelerate the hydrogen evolution of Ni (111) deposition. Chi-Chang Hu [27] reported that the Ni coating from a Watts bath with Ni (111) preferred orientation possesses a high activity for hydrogen evolution due to having a large amount of active sites. For one Ni orientation throughout the electrodeposition, there is a dynamic equilibrium between the producing active sites and the corresponding hydrogen evolution. The more rapid the hydrogen evolution is, the more the following active sites can emerge, so that the Ni (111) orientation can be preferably produced more. Moreover, additional XRD shoulder peak is discerned next to the Ni (111) diffraction plane. That is because the Ni grains turn into amorphous a little

![Fig. 3. SEM images of cross sections. (a) M-Ni coating; (b) B-Ni coating.](image)

![Fig. 4. XRD patterns of the Ni coatings.](image)

### Table 2

<table>
<thead>
<tr>
<th></th>
<th>O-Ni coating</th>
<th>M-Ni coating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Sample</td>
<td>Sample</td>
</tr>
<tr>
<td>Thickness (μm)</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Vickers hardness (Hv0.05)</td>
<td>548.6</td>
<td>574.8</td>
</tr>
</tbody>
</table>

The coating thicknesses are all approximate. Error bars: −0.1 to +0.1 μm).
under exposure of intermittent ultrasound as the intermolecular forces within the structure are disrupted in the ultrasonic duration.

Furthermore, the average grain size determined from XRD analysis is about 25.1 nm for the O-Ni coating, while that of the M-Ni coating is about 18.3 nm, likewise. It is clear that the ultrasonic introduction into the electrodeposition can refine the grain size. In fact, the ultrasound can result in high potential which increases the density of nucleation site and enhances the nucleation rate, so that the growth spaces among the nucleation sites are obviously decreased. Consequently, the growth of Ni grains was inhibited, resulting in the grain refinement.

3.3. Microhardness

The microhardness results are shown in Table 2. It can be seen that the microhardness of both Ni coatings is increased with the increment of the coating thickness, and the microhardness of the M-Ni coating is higher than that of the O-Ni coating. It results from the grain size and the multilayered microstructure. The grain size of the M-Ni coating is smaller than that of the O-Ni coating. Furthermore, the microhardness has been found to follow the Hall–Petch relationship \( H = H_0 + k/d^{1/2} \), where \( d \) is the average grain size, \( H_0 \) is the rule of mixture hardness and \( k \) is a constant. As we all know a small grain size can support a dislocation pileup, which leads to the yield stress increment. Moreover, the interfaces with different elastic constants and different grain sizes are considered to serve as a barrier to dislocations. A sequence of layers is piling up the dislocations in a different manner of multilayered microstructure and thus obstructing dislocation movement between the layers [28].

3.4. Adhesion performance

The adhesion test results are shown in Table 3. It can be seen that bending cycles of the M-Ni coatings to the substrate are about 3 times as many as that of the O-Ni coatings. It is clear that the adhesion of the M-Ni coating to the substrate was enhanced by the microstructure modification. It is well known that the adhesion performance between Ni and Ni should be superior to that between Ni and Fe. However, the interfacial cohesive status is observed from Fig. 3b, where the combination state between the U-Ni layer and the stainless steel substrate is better than that between the O-Ni layer and the U-Ni layer. This means that the surface energy is activated by the ultrasonic agitation, so that adhesion performance of (U-Ni layer)/(O-Ni layer) is superior to that of (O-Ni layer)/(U-Ni layer). Hereby, better integrated adhesion performance can be embodied for the M-Ni coating than that for the O-Ni coating. On the other hand, the formation of multilayered microstructure is also effective to release the stress across the interface of the Ni coating and the substrate. A lower stress gradient at the transition area of the coating/substrate system may account for the enhancement of adhesion [29,30].

3.5. Wear behavior

Fig. 5 shows the results of wear test. From Fig. 5, it can be clearly observed that mass loss of the M-Ni coating is lower than that of the O-Ni coating. This indicates that wear resistance of the Ni coating can be improved by the multilayered microstructure. One interpretation is that the adhesion of the M-Ni coating to the substrate is greatly enhanced as mentioned above. Therefore, the anti-detachment behavior of the M-Ni coating is better than that of the O-Ni coating.
Another interpretation may be ascribed to the multilayered microstructure. It is reported that coating with multilayered microstructure is valid to inhibit the formation of cracks running through the coating [31,32], sometimes further down into the substrate. Moreover, the wear curve slope of the M-Ni coating tends to slow down after 1800 cycles. This means that the nearer the coating to the substrate is, the better its wear resistance is. The reason is due to the multilayered microstructure and the adhesion performance of the coating, which can tally with the results of Table 3. The thinner the coating is, the better the adhesion is. However, the curve slope is unchangeable for the O-Ni coating, since its microstructure is columnar grain, so that its mass loss per cycle is about the same.

The grooves of both Ni coatings in different cross sections were observed after 600 cycles by SEM, and their representative morphologies are shown in Fig. 6. Pit damage in the O-Ni coating can be seen in Fig. 6a along the wear direction, while no such pit damage can be observed in Fig. 6b for the M-Ni coating. Moreover, the grooves of both Ni coatings in different cross sections were also observed after 1500 cycles, shown in Fig. 7. In Fig. 7a, bulk damage along the groove can be seen. It is the representative detachment mode of the columnar grains that the detachment is usually along the columnar grain boundary which was opened up as a result of the bulk-flaking action inevitably.

However, it can be seen that the coating detached from the sixth layer under the surface in Fig. 7c (higher resolution for the framed zone in Fig. 7b), which is a kind of the so-called micro-area detachment. That is because the multilayered coating is a laminated system whose structure is one soft layer and one hard layer in alternation. The dispersed internal stress distribution is caused by the multilayered microstructure, which leads to a gradual breakdown of the friction force layer by layer, so that its anti-detachment behavior is modified. One soft layer plays the role of the shear zone, from which the upper layers easily slide and flake off.

Fig. 8a and b presents the worn surface morphologies of both Ni coatings, and Fig. 8c and d displays the partial zones in Fig. 8a and b at a higher resolution, respectively. As shown in Fig. 8a, pits of bulk flake-off (arrowed) can be clearly observed on the worn tracks. The crack patterns which insert the worn grooves unparallelly indicate that the O-Ni coating has been completely fractured, while no such unparallel grooves can be observed in Fig. 8b for the M-Ni coating. This kind of initial cracks generated on the worn surface is ascribable to the ductility and low hardnnes of the O-Ni coating. Because low-hardness coatings easily yield to the out force, the long crack vertical to the sliding direction can be formed as fatigue crack during sliding (the middle of Fig. 8c). The propagation of these cracks in the coating accelerates the material removal, corresponding to the fatigue wear mechanism [33]. Once this kind of crack was produced, the strain accumulation and the presence of the adhesive forces would spread into the gaps and subsequent delamination, and final peeling appeared. The scar surface profile of the O-Ni coating shows plenty of large debris in Fig. 8c, while fewer and smaller debris can be observed in Fig. 8d. When the wear wheel starts to slide on the sample surface, the sliding-originated surface tensile stresses promote cracks together with the produced debris. With regard to the wear mechanism, it can be described as a “transfer” mode [34], in whose case the interfacial bonding between the sliding pairs is stronger than the cohesive strength, so piece material can be transferred to the counterpart surface progressively. In this way, large sheet-like debris is observed on the worn track for the O-Ni coating, which was produced probably by microdefects of the columnar grains and low hardness. The grooves and debris are indicative of abrasive and adhesive wear modes, respectively. Such a wear mechanism is due to the lower hardness, which could not bear load. All the above discussions indicate that wear mechanism of the O-Ni coating consists of the fatigue and adhesive wear.

In the case of the M-Ni coating, the volume of wear damage obviously reduces, as shown in Fig. 8b, invisible of the bulk-flaking behavior. It only reveals a few small debris and smooth grooves on the sample surface (Fig. 8d), and no fatigue crack was observed. The main reasons are the high hardness and the stress shielding effect caused by the multilayered microstructure. Previous study [35] reports that the multilayered microstructure can reduce the effective stress amplitude in the coating, i.e. the stress shielding effect. The multilayered microstructure considerably increases the compatibility between the coating and the substrate. This
significantly breaks up the stress concentration at the coating/substrate interface and results in higher inhibitions to cracking and delamination. The load-bearing capability is considerably reinforced by the increasing of dislocation densities, which is another reason. It is believed that high dislocation densities enhance the resistance to the growth of wear cracks from the surface into the coating. Under these circumstances, its wear mechanism is the unsophisticated adhesive wear. It is of great significance that the multilayered microstructure inhibits the bulk-flaking behavior. The multilayered microstructure eliminates the pinhole defect, caused by the columnar grain for the ordinary coatings, making the mechanism of coating failure change aggressively.

4. Conclusions

In the present study, the M-Ni coating has been successfully prepared by ultrasound-assisted electrodeposition. Based on the results, the M-Ni coating showed the superior wear resistance than the O-Ni coating due to its multilayered microstructure. And its wear mechanism is adhesive wear. By contrast, the O-Ni coatings failed quickly under wear conditions owing to the microstructure of the columnar grain with poor adhesion and low microhardness. And its wear mechanism is the compound fatigue and adhesive wear. To sum up, the multilayered microstructure removes the defect of the columnar grains in the O-Ni coatings, making the mechanism of coating failure transform enormously under the wear conditions.

Acknowledgments

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References