Tribocorrosion Behavior of Nanocrystalline Metals—a Review

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Nanocrystalline metal materials with ultra fine grains have many special mechanical, physical and chemical properties. Tribocorrosion is a material degradation or transformation process due to the combined action of wear and corrosion. Nanocrystalline materials could be obtained by artificial preparation or tribological/tribocorrosion process. In this paper, studies about the wear, corrosion and tribocorrosion behavior of nanocrystalline metal materials are reviewed. Nanocrystallization could enhance the wear resistance of materials by increasing the hardness and decrease the corrosion rate by forming continuous and compact passive layer. And the nanocrystallization could also enhance the tribocorrosion resistance of materials mainly by increasing surface hardness and forming protective and lubricating surface layers.


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1. Introduction

Nanocrystalline metal materials with ultra fine grains (grain size < 100 nm) have many special performances when compared with conventional coarse-grained metal, such as high hardness and high strength,1–3 enhanced physical properties,4,5 improved tribological properties,6–8 improved corrosion resistance9) and superplasticity at low temperatures,10) etc. These properties arouse the interest and researchers have been conducting wide studies on nanocrystalline materials.

Research on tribocorrosion is a relatively new area that combines the science of tribology and corrosion. These two areas are of major significance and interest in mechanical systems, particularly which are exposed to chemical environment. The phenomena studied are material deterioration processes and transformations caused by the combined effect of wear and corrosion. Wear is a mechanical material degradation process occurring on rubbing or impacting surface while corrosion involves chemical or electrochemical reactions. The synergy effect of these two processes can result in an acceleration of the degradation of materials and finally lead to the failure of materials.11,12)

Because nanocrystalline materials have special microstructures, the tribocorrosion behavior shows apparent differences with coarse grained materials. And the nanocrystalline technology may have huge potential value to enhance the tribocorrosion resistance of materials. However related studies are still lacking. Therefore this paper is written to review recent results of the tribocorrosion behavior of nanocrystalline metal materials.

2. Production of Nanocrystalline Metal Materials

2.1 Artificial preparation

Up to now, the main preparation methods of nanocrystalline metal materials contains in-situ compaction,1) mechanical milling/ alloying,1,3,14) severe plastic deformation,15) electrodeposition,16) powder metallurgy17) and amorphous alloy crystallization.18)

The in-situ compaction method is the earliest way to prepare nanocrystalline metals. But the materials prepared by this method showed a larger porosity and the process is relatively expensive.5) In addition, the mechanical milling method would bring impurity to the production in the ball milling process.19)

Electrodeposition is a widely used method to prepare many kinds of materials including nanocrystalline material. In the electrodeposition process, the current, bath temperature and electrolyte could be justified to reduce the grain size.20) Electrodeposition is a low-cost preparation method, so it has promising potential in the practical application.

Severe plastic deformation is the method to refine the bulk materials surface crystalline to nanometer size. The key point for realizing the surface self-nanocrystallization of a bulk material is to introduce a large amount of defects in to the surface layer so that its microstructure can be transformed into nano-sized crystallites. Mechanically-induced plastic deformation is an effective way to realize the surface self-nanocrystallization on metal materials.21) Recently, Lu et al. have developed two techniques which are based on the severe plastic deformation methods to prepare nanocrystalline materials: surface mechanical attrition treatment (SMAT)15) and surface mechanical grinding treatment (SMGT).22) There are some other new methods, such as powder metallurgy, to prepare nanocrystalline materials and they are not discussed in this paper.

2.2 Naturally formed in tribocorrosion process

In the tribocorrosion process, the surface grain would be refined by the mechanical effect and forming nanocrystalline layer23) and this layer would have an effect on the wear and corrosion behavior of the materials.24) Büscher and Fischer25) reported the wear behavior of four biomedical FCC alloys in the Ringer solution and distilled water. The results showed that there were nanocrystalline layers formed under the worn surfaces of all four alloys. This layer can be generated by the steady strain field directly under the worn surface which brings about a constant sequence of deformation and recrystallisation.26) And in their later works,27) needle epsilon-martensite and twin were found under the worn surface of Cr29Co6Mo alloy. The authors thought that these lattices

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defected reacted with each other under the high shear strain forming rhombic cell. And the dynamic recrystallization can be achieved by two mechanisms which are supposed to act simultaneously. One is at the top surface—by rotating clusters of atoms—within a “mechanically mixed” zone and the second is within the bulk—by the shearing of cells generated by stacking faults and ε-martensite needles—moving towards the surface with the increasing strain gradient. Hesketh et al. also reported similar results.28)

Perret et al.23) also found a refined grain layer under the stainless steel during tribocorrosion in sulphuric acid. Figure 1 shows the longitudinal (parallel to the sliding direction) cross section of wear track.23) There are three subsurface zones from the bottom to the top: the undeformed bulk material, the plastic deformed layer with strain gradient and the mixed nanocrystalline surface layer. And the micro-hardness of nanocrystalline surface reached to 344 ± 7 HV and much higher than the outside of the wear area (140 ± 11 HV). But the authors did not investigate the influence of the nanocrystalline surface to the tribocorrosion behavior.

3. Tribocorrosion Behavior of Nanocrystalline Materials

3.1 Wear

Wear is a mechanical material degradation process occurring on rubbing or impacting surface and wear property is one of the most important application properties of materials. Generally, high strength and hardness could enhance the wear property of materials.6,29) For the remarkable strength and hardness, nanocrystalline materials may have better wear resistance than the conventional coarse grain materials.

Li et al.30) fabricated a nanocrystalline surface layer on medium carbon steel by using high-energy shot peening (HESP) and investigated its tribological behavior. After treated by HESP, the surface hardness increased from about 255 HV to about 513 HV. Figure 2 shows the evolution of friction coefficient and the weight loss due to wear process from the untreated and treated samples as a function of applied loads.30) When the load ranges from 10 to 40 N, the wear weight loss of the as-treated sample was much smaller than that of the original one, while its wear resistance decreased when the tested load exceeded 40 N. The authors thought the wear mechanism of nanocrystalline surface was abrasive wear under low and middle loads and the wear resistance of steel could be improved by the hardened nanocrystalline surface layer. But under high load, the dominant wear mass loss was caused by plastic removal and surface fatigue fracture. The nanocrystalline surface layer would be worn out and the wear resistance reduced significantly.

Besides, Wasekar et al.31) found that the wear loss rate of nanocrystalline Ni coating would decrease with the decreasing of the grain size. They prepared three Ni coatings with different grain size (195 nm, 42 nm and 21 nm) on a mild steel by using pulsed electrodeposition and compared the sliding wear behaviors of these three samples with the bulk Ni (grain size was 43 µm). Figure 3 is the friction coefficient and steady state wear rates of the samples with different grain size.31) The sliding wear rate and coefficient of friction of Ni decreased substantially with decreasing grain size. It indicated that the sample with the smallest grain size has the best wear resistance. And the author also found the worn surface roughness and the size wear debris decreased with decreasing in the gain size.

Sun et al.32) fabricated a nanocrystalline surface layer with an average grain size of 30 ± 5 nm generated by SMAT on AZ91D Mg alloy and investigated the tribological behavior under dry sliding conditions. The result showed that the wear resistance was enhanced by the nanocrystalline layer.

The presented reports indicated that the nanocrystalline materials had better wear resistance than the conventional coarse grain materials. The main reason was that the nanocrystallization of materials could enhance the strength
Fig. 3 The friction coefficient and steady state wear rates of the Ni with different grain sizes.

and hardness, and improve the wear resistance by blocking or reducing the abrasion, surface fatigue and plastic deformation.

3.2 Corrosion

Corrosion is one of the most common reasons that can lead to the failure of metal materials. It would not only bring the loss of the resource but also increase the potential safety hazard. In order to enhance the corrosion resistance of materials, many methods were developed, such as changing the composition and microstructure, using inhibitors, and fabricating coatings. Because the special microstructure, nanocrystalline materials show difference in corrosion behavior as well as in mechanical performance with the coarse grain materials.

Oguzue et al. studied the corrosion properties of a nanocrystalline low carbon steel coating (SNCLCS, grain size was about 40 nm) fabricated on a low carbon steel substrate by magnetron sputtering and the bulk steel (BLCS) in aerated 0.5 M H₂SO₄ solution by EIS and polarization techniques. The results showed that the nano-grained microstructure accelerated the corrosion rate of low carbon steel in the acidic environment by shifting the corrosion potential to more negative (active) values and increasing the kinetics of the anodic reaction. Qin et al. prepared nanocrystalline and coarse grain Ni with different grain sizes (from 16 nm to 2 µm) by using the direct current electrodeposition and investigated the effect of grain size on the electrochemical corrosion behavior in different corrosive media. They found that the decreasing of the grain size did not always lead to the increasing of the corrosion rate. Table 1 is the corrosion potential and the corrosion current density of Ni deposits obtained from electrochemical polarization curves in different corrosive media. In NaOH and NaCl solutions, the decreasing of the grain size shifted the corrosion potential to positive values and decreased the corrosion current density that indicated that the nanocrystalline Ni with smaller grain size exhibited improved corrosion resistance in comparison with coarse-grained Ni. But in the H₂SO₄ solution, the corrosion resistance of nanocrystalline Ni deposits decreased with decreasing grain size. The authors thought that the decreasing of the grain size increased the grain boundary density, which could accelerate the formation of continuous and protective passive films in NaOH and NaCl solutions. However there was no passive process in H₂SO₄ solution. The corrosion resistance of nanocrystalline Ni decreased with the decreasing of the grain size.

From the above reports, nanocrystallization has obvious influence on the corrosion behavior. The nanocrystallization could change the surface condition of metals, which effectively increasing the activity of metallic atoms, the density of nucleation sites for forming the passive film and accelerate the corrosion reactions. Therefore, if the corrosion products are soluble, the corrosion rate would increase by nanocrystallization. If the corrosion products are insoluble, the nanocrystallization could form more continuous and compact passive layer to protect the metal.

### Table 1 Corrosion potential and corrosion current density of Ni deposits obtained from electrochemical polarization curves in different corrosive media.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Grain size</th>
<th>Corrosion potential (vs SCE)/V</th>
<th>Corrosion current density (µA cm⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>16 nm</td>
<td>−0.429</td>
<td>0.57</td>
</tr>
<tr>
<td>1% NaOH</td>
<td>93 nm</td>
<td>−0.470</td>
<td>0.79</td>
</tr>
<tr>
<td></td>
<td>258 nm</td>
<td>−0.530</td>
<td>0.90</td>
</tr>
<tr>
<td></td>
<td>2 µm</td>
<td>−0.617</td>
<td>1.69</td>
</tr>
<tr>
<td>3% NaCl</td>
<td>16 nm</td>
<td>−0.494</td>
<td>5.21</td>
</tr>
<tr>
<td></td>
<td>93 nm</td>
<td>−0.462</td>
<td>7.55</td>
</tr>
<tr>
<td></td>
<td>258 nm</td>
<td>−0.401</td>
<td>15.89</td>
</tr>
<tr>
<td></td>
<td>2 µm</td>
<td>−0.325</td>
<td>53.43</td>
</tr>
<tr>
<td>1% H₂SO₄</td>
<td>16 nm</td>
<td>−0.084</td>
<td>45.19</td>
</tr>
<tr>
<td></td>
<td>93 nm</td>
<td>−0.116</td>
<td>16.78</td>
</tr>
<tr>
<td></td>
<td>258 nm</td>
<td>−0.184</td>
<td>7.73</td>
</tr>
<tr>
<td></td>
<td>2 µm</td>
<td>−0.313</td>
<td>4.81</td>
</tr>
</tbody>
</table>

3.3 Tribocorrosion

Tribocorrosion is a material degradation or transformation due to the combined action of wear and corrosion. Because of the interaction of chemical and mechanical factors, tribocorrosion is not simply the sum of corrosion and wear taken separately. The most accepted mechanism of tribocorrosion is the “passive film broken” theory. Figure 4 is the schematic illustration of the degradation mechanism of tribocorrosion. When the metal is surrounded with corrosion media, the metal would be corroded and form a corrosion products film (usually consists of oxides and hydroxides) on surface. This passive film could decrease the corrosion rate by blocking the transfer of ion and electron. But under the siding condition, the passive film would be removed which leads to the exposing of highly reactive bare metal to the environment and increasing the corrosion rate (wear accelerated corrosion). On the other hand, corrosion could affect wear as well. For example, passive films may render metal brittle and prone to wear and corrosion products may act as lubricants.

As mentioned above, the nanocrystallization could enhance the wear resistance and decrease or increase the corrosive rates (depending on the property of the corrosion products). So the tribocorrosion behavior of nanocrystalline
Corrosion could also affect the wear process by forming corrosion products. Chen et al.\(^4\) found that the passive film on nanocrystalline Al surface showed increased hardness and high resistance to scratching. Sun and Bailey\(^5\) fabricated a nanocrystalline surface layer on 304 stainless steel by using the SMAF. The coefficients of friction of treated sample with different applied potential (meaning different corrosion characters) were always lower than the untreated sample. And with the applied potential changing from negative to positive, the coefficient of friction fall. At the high potential, the electrochemical reaction was more severe and the passive film or insoluble corrosion products were more easily and adherently form on the nanocrystalline surface and act as lubricant to lower the coefficient of friction.

It is mentioned in the above section that the nanocrystalline surface layer would be naturally formed on the materials in the tribocorrosion process. But this nanocrystalline layer would degrade in the continuous tribocorrosion process. The nanocrystalline layer may go through a dynamic circle: formation → degradation → formation. Mathew et al.\(^24\) investigated the tribocorrosion of CoCrMo alloy with different surface condition. The substrates are undergone electrochemically polishing and mechanically polishing. The mechanically polishing sample formed a thin nanocrystalline surface but the electrochemically polishing surface was same as the bulk substrate. The result showed that the mechanically polished sample had better tribocorrosion resistance than the electrochemically polishing sample. This means that the formation of the nanocrystalline layer may decrease the tribocorrosion rate. Beside, the formation of nanocrystalline layer may lower the coefficient of friction. Papageorgiou et al.\(^5\) reported the tribocorrosion mechanisms of NiCrMo-625 alloy in NaCl solution. They thought that under the tribocorrosion process, there was a lubricating “nanocrystalline tribocorrosion layer” on the surface. Though these researchers have found the nanocrystallization in tribocorrosion process and discuss its affect to tribocorrosion behavior, the real role of the nanocrystallization on tribocorrosion still needs more and deeper investigation.

### 4. Conclusion

Nanocrystalline metal materials with special microstructures have many excellent properties. The nanocrystalline structure could be obtained by some artificial preparations and naturally form in tribocorrosion process. Nanocrystalline materials have different wear, corrosion and tribocorrosion behaviors compared with the conventional coarse-grained materials. The high hardness of nanocrystalline materials could observably enhance the wear resistance. The high density of the grain boundary can effectively accelerate the atomic diffusion and increase the activity of metals, and accelerate the electrochemical reactions to form continuous and compact passive layer or insoluble corrosion products which can decrease the corrosion rate. The nanocrystallization can enhance the tribocorrosion resistance of materials mainly by increasing hardness and forming a protective and lubricating passive film. But the real role of the nanocrystallization on tribocorrosion still needs more and deeper investigation.

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**Table 1**

The volume losses (mm³) of nanocrystalline and microcrystalline Cu deposits in different corrosion solutions.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Sample</th>
<th>V&lt;sub&gt;total&lt;/sub&gt;</th>
<th>V&lt;sub&gt;wear&lt;/sub&gt;</th>
<th>V&lt;sub&gt;corr&lt;/sub&gt;</th>
<th>V&lt;sub&gt;syn&lt;/sub&gt;</th>
<th>V&lt;sub&gt;wear&lt;/sub&gt;/V&lt;sub&gt;total&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>Nano</td>
<td>5768</td>
<td>4508</td>
<td>0.0043</td>
<td>1260.00</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Micro</td>
<td>9441</td>
<td>7153</td>
<td>0.0105</td>
<td>2287.99</td>
<td>0.23</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;SO&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Nano</td>
<td>6357</td>
<td>4655</td>
<td>0.0309</td>
<td>1701.97</td>
<td>0.27</td>
</tr>
<tr>
<td></td>
<td>Micro</td>
<td>9459</td>
<td>7289</td>
<td>0.0132</td>
<td>2160.99</td>
<td>0.23</td>
</tr>
</tbody>
</table>

Where V<sub>total</sub> is the total volume loss, V<sub>wear</sub>, V<sub>corr</sub> and V<sub>syn</sub> are the volume losses caused, respectively, by pure wear, pure corrosion and their synergistic attack.

For the nanocrystalline materials, their high hardness and high density of grain boundary may have significant influence on tribocorrosion behavior. Tao et al.\(^4\) used the pulse-current and direct-current electrodeposition processed to produce nanocrystalline (grain size was ~56 nm) and microcrystalline (grain size was ~2 μm) Cu deposits on brass substrate. The authors investigated the tribocorrosion behaviors of these two deposits in NaOH and H<sub>2</sub>SO<sub>4</sub> solutions. The result (Table 1) showed the nanocrystalline Cu deposit had a high resistance to tribocorrosion than the microcrystalline on in all solutions. It is evident that wear was the main degradation way of deposits and the mechanical action dominated the total materials loss. The synergy of corrosion and wear led to a considerable increase in the materials loss. It is worth to notice that the passive film was strongly affected by the wear-accelerated corrosion. It could be seen that nanocrystalline with a high density of the grain boundary would activate the surface and forms a protective film. Cu has a passive behavior in NaOH solution but not in H<sub>2</sub>SO<sub>4</sub> solution, so the nanocrystalline Cu had lower ratio of V<sub>syn</sub> to V<sub>total</sub> in NaOH solution. The decreasing of the grain size can obviously enhance the tribocorrosion resistance of materials. Even the grain size is smaller than 100 nm, tribocorrosion resistance of nanocrystalline materials could be enhanced further by continuously decreasing the grain size. Hassani et al.\(^20\) prepared four nanocrystalline Ni-Co Coatings with different grain sizes (22 to 46 nm). The coating with the smallest grain size showed the highest HV hardness and the best tribocorrosion resistance.

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**Fig. 4** Schematic illustration of the degradation mechanism of tribocorrosion.
Acknowledgments

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REFERENCES