Microstructure and wear resistance of electrodeposited Ni-SiO$_2$ nano-composite coatings on AZ91HP magnesium alloy substrate

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Abstract: The Ni-SiO$_2$ nano-composite coatings were fabricated by electrodeposition on the AZ91HP magnesium alloy surface, in which nano-SiO$_2$ was chosen as the second-phase particulates. The microstructure was observed by SEM, the microhardness was measured by micro-density tester and the wear resistance was estimated by M−200 type block-on-wheel dry sliding frication and wear tester. The results indicate that the Ni-SiO$_2$ nano-composite coatings with uniform crystalline, dense structure can be obtained on AZ91HP magnesium alloy. The interface morphology shows that the combination between the nano-composite coatings and magnesium alloy is fine. The maximum value of microhardness reaches HV367 when the content of nanoparticles is 10 g/L, however, the microhardness of the pure nickel coatings is HV274 and the hardness of magnesium alloy only is HV82.7. The frication and wear experiments reveal that the wear resistance of nano-composite coatings are improved obviously compared to magnesium alloys and pure nickel coatings, which are induced by dispersive strengthening effect and grain refining effect. The main wear mechanism of nano-composite coating is abrasive wear, the wear mechanism of magnesium alloys is adhesion wear, and that of pure nickel coating is exfoliation wear, respectively.

Key words: magnesium alloy; nano-composite coatings; microstructure; wear resistance

1 Introduction

Magnesium alloy has many prominent characters such as high strength (stiffness) radio, electromagnetic shielding, vibration abatement, superior cutting performance and recoverability. In recent years, magnesium alloy has been developed quickly in the industrialization. Especially, magnesium alloy was applied in aerospace, automotive industry and electronic communications. AZ91HP magnesium alloy has excellent performances of casting process and low-cost, which has become the most widely used casting magnesium alloy. Magnesium has a negative standard potential, so that magnesium alloy is poor corrosion resistant [1]. On the other hand, the hardness of magnesium alloy is low, so that the wear resistance is poor also. Therefore, the application of magnesium alloy is restricted [2]. To improve the properties of magnesium alloy, many surface modification technologies were used, including electroplating, electroless plating [3],

conversion coating [4−5], anodizing [6−9], micro-arc oxidation [10], hydride coating [11], organic/polymer coatings [12−13] and gas phase deposition [14−16]. Especially, the micro-arc oxidation technology, compared with ordinary anodic oxidation, has advantages such as process simple, pollution-free, uniform coating as well as wide materials adaptability, and has become the main protective technology of magnesium alloy. In recent years, the nano-composite electrodeposition technology was used to fabricate new types of nano-composite coating of magnesium alloy [17−18].

In this work, the nano-composite coatings were prepared by composite electrodeposition, and the microstructure and wear resistance were discussed.

2 Experimental

Fabrication process of nano-composite coating was designed as follows: sample preparation — alkaline cleaning—pickling—activating—electroless plating—

nano-composites electrodeposition. After each step, the sample must be washed with water for 1 min to remove the residual liquid of the last process and avoid affecting next process.

AZ91HP magnesium alloy samples with size of 55 mm × 10 mm × 10 mm were cut by electro-discharge (DK7732E). The samples were ground with sandpaper to remove the surface oxide film and other impurities. Electro- deposition equipments were SMD-30 Numerical Control Double Pulse Plating Power Supply, KQ−250DE Numerical Control Ultrasonic Devices and JJ−1 Electric Mixing Machine.

Nano-particles have a very high surface energy and great specific surface area, so are easy to aggregate reunion in the electrolyte. Therefore, nanoparticles aggregation must be effectively solved in the fabrication process. To obtain high dispersion of nanoparticles in the electrolyte, a small amount of dispersing agent was used to fully wet n-SiO_2 at first, then was ultrasonic oscillated for more than 4 h, at was last added in the electrolyte. The ultrasonic oscillation and mechanical mixing were used together in the electrodeposition process. The component and parameters of pretreatment bath were listed in Table 1 and the electrodeposition parameters of preparing Ni-SiO_2 composite coating were listed in Table 2.

Table 1 Component and parameter of pretreatment bath

Component	Value/(g·L^{-1})	Parameter	Value
NaSiO$_4$·6H$_2$O	15	pH	6.4
NaH$_2$PO$_2$·H$_2$O	14	Temperature/°C	82±2
NaC$_2$H$_3$O$_2$	13		
HF (40%)	12		
NH$_4$HF$_2$	8		
Stabilizer	0.001		

Table 2 Electrodeposition parameters of preparing Ni-SiO_2 composite coating

Component	Value/(g·L^{-1})	Parameter	Value
NaSiO$_4$·6H$_2$O	280	Current density/ (mA·mm^{-2})	20−80
NiCl$_2$·6H$_2$O	40		
H$_3$BO$_3$	35	pH	3.5−4.5
Wetting agent	0.1−0.2	Temperature/°C	50−60
Dispersant	0.1−0.5		

3 Results and discussion

3.1 Microstructure of Ni-SiO_2 composite coatings on AZ91HP magnesium alloy surface

Compared with the Ni coating, the sizes of crystal grains in the Ni-SiO_2 nanocomposite coating largely decrease due to the dimension effect of nanoparticles (Fig. 1). The high active surface of nanoparticles provides an amount of nucleus for Ni atoms in the process of electrodeposition. The overpotential of metal forming nucleus reaction decreases. The composite coating with fine and compact microstructure is obtained because of the higher nucleation rate [19]. On the other hand, in the coating deposition process, the nickel polycrystalline modules of predeposition form the microscopic nodular and the phenomenon results in "edge effect", so that the current density increases and deposition rate accelerates, in which the role of feedback loop is produced. The "edge effect" would be hindered due to the diffusion deposition of nano-particles on the coating surface in the electrodeposition process. Moreover, the consecutive growth of nickel metal in the nano-particles deposited position is impeded, so that the crystal plane orientation of original nickel grain occurs to change and turns to new epitaxial growth. With the nano-particles of composite coatings increasing, the nickel crystal plane orientation becomes more littery. The epitaxial growth of nickel grain to larger sizes is impossible in a certain crystal plane orientation, so that the grains of nickel become fine. Therefore, when the surface of AZ91HP magnesium alloy electrodeposition
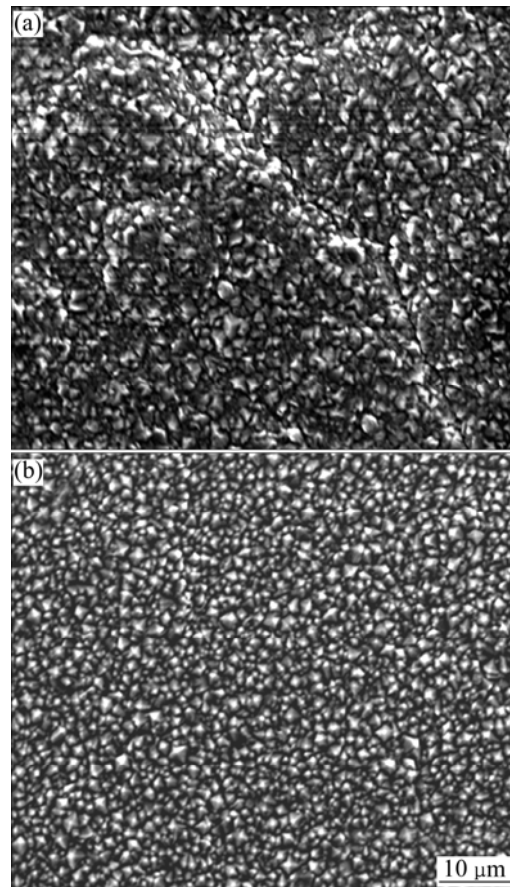

Fig. 1 Microstructures of coating on AZ91HP magnesium alloy: (a) Pure nickel coating; (b) Ni-SiO_2 nano-composite coating

coating was compared to that of the pure nickel, the crystallization of nanocompostie coatings is more uniform and denser.

Figure 2 shows the interface of AZ91HP magnesium alloy and Ni-SiO$_2$ nano-composite coating by SEM. The nano-composite coating is even, compact, with no obvious cracks, holes, and so on. The thickness of composite coating is about 20 μm. The combination between the composite coatings and AZ91HP magnesium alloy is very well.
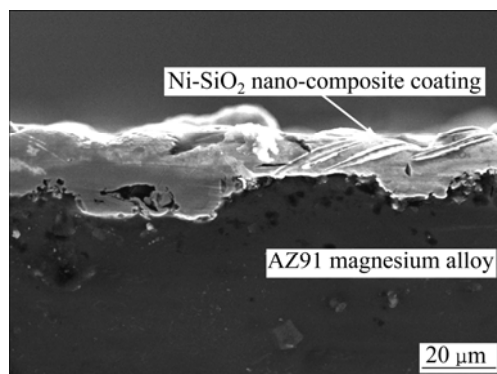

Fig. 2 Interface morphology of Ni-SiO$_2$ nano-composite coating

3.2 Microhardness of Ni-SiO$_2$ composite coating on AZ91HP magnesium alloy surface

Figure 3 shows the microhardness of Ni-SiO$_2$ nano-composite coating with different concentration of n-SiO$_2$ in the electrodeposition bath. The maximum microhardness is HV367 when the content of n-SiO$_2$ is 10 g/L. The reasons are that the nanoparticles have a dispersion strengthening effect, which impede the dislocation movement of metallic matrix and limit grain boundary sliding. Therefore, the microhardness of the composite coatings is enhanced. On the other hand, the nanoparticles as new growth points make the growth rate of the crystal nucleation decrease, which leads to the
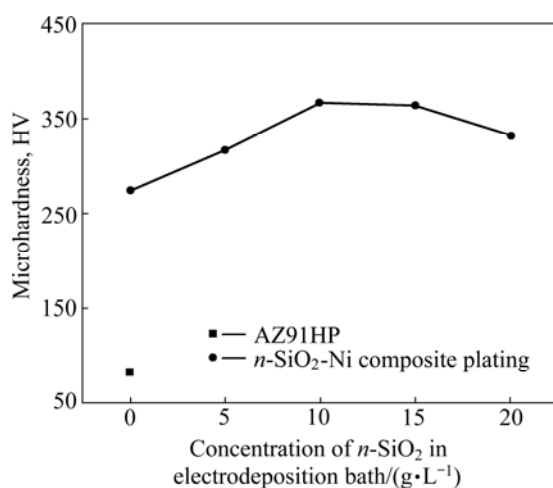

Fig. 3 Microhardness of Ni-SiO$_2$ nano-composite coatings

grain refinement. Therefore, the mechanical properties of composite coating are also improved. Usually, the amount of n-SiO$_2$ suspended in the electrodeposition bath increase with the content of nanoparticles increasing. At the same time, the amount of nanoparticles contained in the coating increases. However, when the content of the nanoparticles increases to a certain extent, the very small nanoparticles are prone to agglomeration due to the specific surface area effect, resulting in the increase of solution viscosity, and hindering the movement of matrix metal plasma so that the deposition rate decreases. Therefore, when the content of nanoparticles in the electrodeposition is high enough, the nanoparticles of composite coating will decrease.

3.3 Wear resistance of Ni-SiO$_2$ composite coatings on AZ91HP magnesium alloy surface

Figure 4 shows the wear morphologies of AZ91HP magnesium alloy, pure nickel coating and nanocomposite coating at low load, respectively. Figure 5 shows the wear morphologies of AZ91HP magnesium alloy, pure nickel coating and nanocomposite coating at high load, respectively. It can be seen that, the wear mechanism of AZ91HP magnesium alloy surface is mainly adhesive wear. In low-load (10 N) wear, the friction pairs generate plowing on the substrate surface (Fig. 4(a)). With the load (30 N) increasing, the plowing is deepened and widened on the surface of AZ91HP magnesium alloy. The material surface generates elasto-plastic deformation, accompanied with repeated plastic deformation, leading to surface cracks. With the friction continuing, the temperature gradually increases, and the surface adhesion wear becomes obvious. These adhesive friction points have been cut in the friction course, thus form adhesive wear (Fig. 5(a)).

The wear surface of the pure nickel coating at low-load (10 N) is flat, but there are some grooves parallel to the direction of friction pairs movement and the grooves are shallow (Fig. 4(b)). In sliding wear process, the interface parts will be the first occurrence of fatigue damage due to repeated shear stress. When the accumulation of fatigue damage reaches to a certain extent, the microcracks are formed. The macrocracks are formed due to the microcracks expanding and connection under cyclic stress. At the same time, these macrocracks expand toward the material weakness. With the load (30 N) increasing, the macrocracks expand continually. When the intensity factor (K_{max}) of the crack tip stress is gradually close to the material fracture toughness (K_c), the cracks will occur with a sharp local buckling, which behave as being cut (Fig. 5(b)). Therefore, large areas exfoliation occur at the cracks parts of the pure nickel coating [20], which is a typical exfoliation wear.

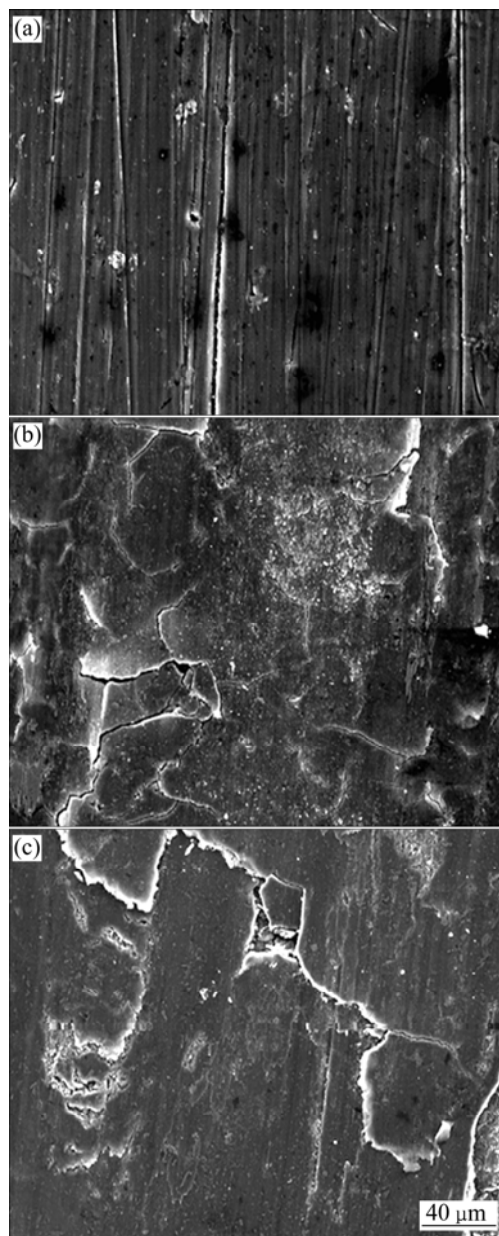The wear surface of nano-composite coating is not

Fig. 4 Wear surface morphologies at low load (10 N): (a) Magnesium alloy; (b) Pure nickel coating; (c) Nano-composite coating

Fig. 5 Wear surface morphologies at high load (30 N): (a) Magnesium alloy; (b) Pure nickel coating; (c) Nano-composite costing

only flat at low-load (10 N), but also grooved parallel to the direction of friction pairs movement, and the grooves are shallow, which are similar to pure nickel coating. But the amount of cracks is less than that of pure nickel coating obviously (Fig. 4(c)). With the load (30 N) increasing, grooves are deepened on the wear surface of composite coating and appear small wear debris. But there are no large areas exfoliation phenomenon, and wear debris will be involved in the wear process, where wear mechanism is a typical abrasive wear (Fig. 5(c)). Therefore, the wear resistance of composite coating is improved obviously. The main reasons are nanoparticulate grain refining and dispersive strengthening effects. The
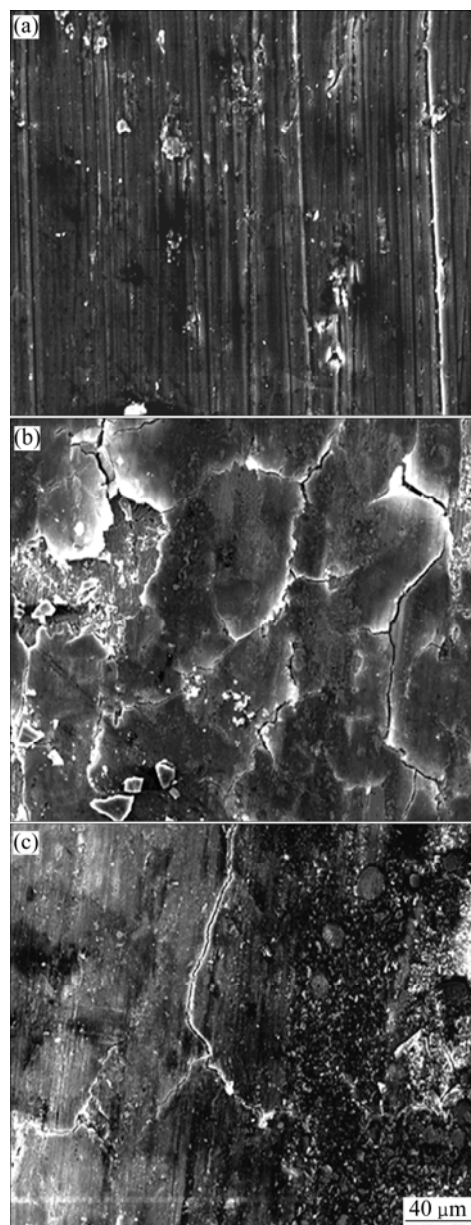
nanoparticles uniformly distribute in the composite coating, and serious distortion occurs near the nanoparticles. At the same time, the defects increase, the nickel matrix dislocations movement and deformation are hindered. Therefore, the hardness and strength of the coatings significantly increase [21−23]. In the friction process, the nanoparticles embedded in the composite coating are exposed gradually in the contact surface, and play a load-bearing role, which inhibit the expansion and peeling of the adhesion areas and strengthen the adhesive wear resistance [24−26]. The wear mechanism of nanocomposite coating is abrasive wear, which is superior to wear resistance of pure nickel coating.

4 Conclusions

1) Sulfate salts were used as pretreatment of electroless plating process. Electrodeposition was used to fabricate Ni-SiO$_2$ nanocomposite coatings on the AZ91HP magnesium alloy.

2) The Ni-SiO$_2$ nanocomposite coatings with uniform crystalline, dense structure are obtained on the AZ91HP magnesium alloy. The interface morphology shows that the combination between the nanocomposite coatings and magnesium alloy is fine.

3) The maximum value of microhardness reaches HV367 when the content of nanoparticles is 10 g/L, which is higher than that of pure nickel coatings and magnesium alloy. The frication and wear experiments reveal that the wear resistance of nanocomposite coatings are improved obviously compared to the magnesium alloys and pure nickel coatings, which are induced by dispersive strengthening effect and grain refining effect. The main wear mechanism of nanocomposite coating is abrasive wear, the wear mechanism of magnesium alloys is adhesion wear, and that of pure nickel coating is exfoliation wear, respectively.

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AZ91HP 镁合金电沉积 Ni-SiO₂ 纳米复合镀层的显微结构与耐磨性

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摘　要：以 AZ91HP 镁合金为研究对象，以纳米氧化硅为第二相粒子，通过纳米复合电沉积法制备 AZ91HP 镁合金 Ni-SiO₂ 纳米复合镀层。利用扫描电镜观察纳米复合镀层的显微形貌与微观结构，利用显微硬度计测定纳米复合镀层显微硬度，利用 M−200 摩擦磨损试验机测试纳米复合镀层的耐磨性能。结果表明：在 AZ91HP 镁合金表面获得了结晶均匀、结构致密的 Ni-SiO₂ 纳米复合镀层；纳米复合镀层剖面形貌显示纳米复合镀层与镁合金基体结合良好；镀液中纳米颗粒含量为 10 g/L 时，AZ91HP 镁合金表面电沉积 Ni-SiO₂ 纳米复合镀层的显微硬度最高，最高达 HV367；摩擦磨损试验表明纳米复合镀层与镀镍层、镁合金基体相比，耐磨性明显提高，这是由于纳米颗粒的细晶强化和弥散强化所致；纳米复合镀层的磨损机制主要是磨粒磨损，镁合金基体磨损机制为粘着磨损，镀镍层磨损机制为剥层磨损。
关键词：镁合金；纳米复合镀层；显微结构；耐磨性

(Edited by LONG Huai-zhong)