Analysis and Development Review of Metal and Metal/Ceramic Composite Coating Prepared on Magnesium Alloy Surface

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Abstract. Magnesium, as one of the lightest metal structural materials, also has its advantages such as high specific strength, good electromagnetic shielding characteristics, good processability and easy recycling, so it has a wide application prospect. However, its poor insulation, corrosion resistance, wear resistance and other properties limited it to be an alloy that can be used in a large area. Therefore, how to improve the corrosion resistance and wear resistance of magnesium alloy is the key to promote the development of magnesium alloy field. This paper reviews the research progress of using magnetron sputtering technology to prepare ceramic composite film on the surface of magnesium alloy and briefly introduces the film corrosion resistance and wear resistance of the thin films. It analyzes the impact of metal transition layer, process parameters and other factors on structure and properties of metal / ceramic coatings and prospects for the development prospects of magnetron sputtering in the field of magnesium alloy surface protection.

Keywords: Magnetron Sputtering, Magnesium Alloy, Composite Film, Corrosion Resistance, Wear Resistance.

Foreword
The main problems that mankind facing in the 21st century are environmental pollution and resource starvation. Reducing the increasingly serious environmental pollution and saving resources is one of the technical challenges in the new century [1-2]. As the eighth most abundant element on the earth and the third most abundant element in seawater, the usage of Magnesium in engineering materials is second only to steel and aluminum. Besides, Magnesium, as one of the lightest metal structural materials, also has its advantages such as high specific strength, good electromagnetic shielding characteristics, good processability and easy recycling, etc. With the continuous improvement and maturity of magnesium alloy production technology, magnesium alloys are increasingly widely used in various fields. However, due to the high electrochemical activity, it leads to extremely low corrosion resistance of magnesium alloys. Besides, the unsatisfactory wear resistance of magnesium alloys causes its only use in static components. Summary, the poor corrosion resistance and wear resistance of magnesium alloys prevent it from becoming a widely used alloy. Therefore, how to improve the corrosion resistance and wear resistance of magnesium alloys is one of the emphases for research of domestic and foreign scholars [3].

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Surface protection technology is one of the most effective methods to protect magnesium alloys from corrosion and wear. At present, various methods have been applied to the surface protection of magnesium alloys, including chemical conversion treatment, anodic oxidation treatment, microarc oxidation treatment, etc. However, each of these methods have their respective merits and demerits. For example, the chemical conversion treatment is to form a stable compound film on the surface through the chemical reaction of the magnesium alloy and the treatment liquid. However, this process causes great pollution to the environment during the treatment process, which is not compliant with green environmental protection; Anodic oxidation treatment refers to the surface protective technology in which a layer of oxide film is formed on the surface of magnesium alloy in electrolyte solution under the electrolysis. Although this process can reach the aim of big area sedimentation to accumulate thin films and dealing with parts with complex shapes, the mechanical properties of the films are poor. Magnetron sputtering, as a deposition method of physical vapor deposition (PVD), can deposit wear resistant, corrosion-resistant, optical and other functional films, and has the advantages of low cost, strong adhesion with substrate, high deposition rate and green environmental protection, which other traditional technologies cannot be compared with. Therefore, magnetron sputtering, as one of the mainstream coating technologies, is one of the main means for the green development of thin film industrialization.

At present, the research on the surface modification of magnesium alloys by magnetron sputtering at home and abroad is mostly focused on different film structures and materials. Common thin film materials include metals, ceramics and polymers. Metal thin film materials have physical properties such as electrical conductivity, thermal conductivity, high hardness, and high melting point, which have always been a hot research topic. The corrosion resistance, wear resistance and good insulation effect of ceramic film materials are also deeply concerned by researchers. The ceramic film on the surface of magnesium alloy is easy to peeled off, because of the mismatching between magnesium alloy and ceramic film. Therefore, researchers tried to introduce a transition layer between the ceramic film and the magnesium alloy to form a composite coating. The main purpose of the transition layer is to increase the film-base bonding force and reduce the porosity caused by the PVD process. This article reviews the research progress of ceramic composite coatings on magnesium alloy surfaces, briefly analyzes the influencing factors of corrosion resistance and wear resistance of different types of films, and prospects for the development prospects of magnetron sputtering in the field of magnesium alloy surface protection.

1. Magnetron Sputtering Metal/ceramic Composite Coating on Magnesium Alloy Surface

Due to the rapid development of industry, higher requirements are put forward on mechanical parts, and the corresponding performance requirements for materials are getting higher and higher, such as high temperature resistance, wear resistance, and corrosion resistance [4]. Since ceramic materials have corrosion resistance and wear resistance that metal materials are incomparable, combining metal and ceramic materials on the surface of magnesium alloys can be applied in a wider range of fields. In recent years, researchers have used magnetron sputtering to prepare different types of coatings on the surface of magnesium alloys. Since metal/ceramic composite coatings can improve the corrosion resistance and wear resistance of magnesium alloys, and can solve the matching problem of ceramic materials and magnesium alloy substrates, metal/ceramic composite coatings have always been a research hotspot.

The metal/ceramic composite coating is composed of a metal layer and a ceramic layer as a dual-type coating structure system. The metal layer as a transition layer acts as a connecting medium between the ceramic layer and the magnesium alloy substrate in the metal/ceramic composite coating structure. Its main purpose is to increase the bonding strength of the ceramic layer and the magnesium alloy substrate and reduce the porosity of the coating to ensure the ceramic the function of the coating, thereby improving its performance. Since the structure and performance of the metal/ceramic composite coating are easily affected by other factors such as the metal transition layer and the preparation process, the researchers have conducted related studies.
1.1 The Effect of Metal Transition Layer on the Corrosion and Wear Resistance of Metal/Ceramic Composite Coatings

The corrosion resistance of the metal/ceramic composite coating is greatly affected by the metal transition layer. In the protection mechanism of the metal/ceramic composite coating, when the outer ceramic layer fails, whether the coating can effectively protect the substrate depends on the material properties of the transition layer, the microstructure and the bonding strength between the transition layer and the substrate. Therefore, in addition to the surface ceramic coating, the transition metal layer also plays an important role. It is easy to find from Table 1 that the corrosion resistance of the magnesium alloy samples coated with the metal/ceramic composite coating has been significantly improved compared to the magnesium alloy matrix. Guosong Wu et al. compared the corrosion resistance of $\text{Al}_2\text{O}_3$/Al and $\text{Al}_2\text{O}_3$/Ti composite coatings on the surface of AZ31 magnesium alloy under the same deposition conditions. They found that the corrosion current density of $\text{Al}_2\text{O}_3$/Al film is far much lower than $\text{Al}_2\text{O}_3$/Ti film. The reason is that the corrosive medium can contact the substrate through the coating defects, causing the metal transition layer and the substrate to form a corrosion battery. Since the surface of the transition layer Al can form a dense layer of alumina, which matches well with the ceramic layer $\text{Al}_2\text{O}_3$, the $\text{Al}_2\text{O}_3$/Al composite coating is not easy to be damaged. In addition, the immersion test results show that the surface of the $\text{Al}_2\text{O}_3$/Ti film sample after immersion for 2 hours has been corroded in many places, and the corrosion pits are relatively deep, while the corrosion degree of the surface of the $\text{Al}_2\text{O}_3$/Al film is less than that of the $\text{Al}_2\text{O}_3$/Ti film test sample. Therefore, the corrosion resistance of $\text{Al}_2\text{O}_3$/Al coating is better than that of $\text{Al}_2\text{O}_3$/Ti coating. At the same time, the scholar studied the effect of the intermediate layer (Ti, Al) on the corrosion resistance of the composite coating under the simulated physiological environment, and found that the Ti intermediate layer accelerates the corrosion rate of the magnesium alloy, and the addition of the aluminum intermediate layer makes the $\text{AlOxNy}$ coating more effective. The surface mechanical properties have been slightly improved, but it can effectively prevent corrosion. The results show that the aluminum intermediate layer is better than the titanium intermediate layer [13].

Table 1. Corrosion resistance of metal/ceramic composite coating on magnesium alloy

| Metal | Ceramic layer | Matrix | $E_{corr}$/V | $I_{corr}/(\mu\text{A}\cdot\text{cm}^{-2})$ | references |
|-------|---------------|--------|--------------|---------------------------------|------------|
| Al    | AlN/DLC       | AZ31   | -1.527       | 89.1                            | [5]        |
| Al    | $\text{Al}_2\text{O}_3$ | AZ31 | -1.48 | 1.28 | [5] |
| Al    | $\text{AlO}_x\text{N}_y$ | AZ31 | -1.614 | 0.3154 | [6] |
| Al    | SiN$_x$       | AZ31   | -1.501       | 13                              | [7]        |
| Ti    | TiN/TiC$_x$N$_{1-x}$ | AZ31 | -1.129 | 0.707 | [8] |
| Ti    | SiN$_x$       | AZ31   | -1.282       | 0.88                            | [7]        |
| Zr    | SiN$_x$       | AZ31   | -1.559       | 0.24                            | [7]        |
| Zr    | AlTiN         | AZ31   | -1.563       | 1.248                           | [10]       |
| Al    | TiAlN         | AZ91   | -1.570       | 162.7                           | [11]       |
| Hf    | Si$_3$N$_4$   | AZ91   | -1.578       | 2.798                           | [12]       |
| Hf    | HfN           | AZ91   | -0.51        | 0.01                            | [13]       |
| Mg    | TaO           | ZK60   | -1.552       | 77.393                          | [9]        |

In addition to acting as a good bonding medium, the metal transition layer in the metal/ceramic composite coating should also have a certain bearing function, which can further improve the overall wear resistance of the composite coating. Table 2 lists the wear resistance of the magnetron sputtering metal/ceramic composite coating on the surface of the magnesium alloy. Xiaojing Xu et al. [14]
prepared Ti/SiC/CNx composite coatings on the surface of magnesium alloys by room temperature magnetron sputtering technology. The study showed that the metal transition layer Ti played a certain role in the high wear resistance of the composite coatings. This is because the metallic titanium layer provides a good interface bond between the coating and the substrate, and can provide better support for the ceramic layer to avoid the substrate from being too soft and cracking. Zeliang Ding et al. [9] prepared Mg/TaO composite coatings on the surface of magnesium alloys by magnetron sputtering process, effectively decrease the interface stress between the ceramic layer TaO and the magnesium alloy substrate is reduced, and the bonding force of the coating system is improved. Jiamu Huang et al. [10] deposited SiNx ceramic coating and Zr(Al,Ti)-SiNx composite coating on the surface of magnesium alloy, and found that the adhesion of composite coating to magnesium alloy was better than that of SiNx ceramic coating, indicating that the metal transition layer can increase the adhesion of the composite coating to the substrate. And the adhesion of the Al/SiNx composite coating is level 2, and the adhesion of the Ti/SiNx composite coating is level 1, indicating that the metal Ti transition layer is better than Al in improving the adhesion of the film base. Guosong Wu et al. compared Al2O3/Al and Al2O3/Ti two composite films on the surface of AZ31 magnesium alloy under the same deposition conditions. They found that compared with Al2O3/Al film, Al2O3/Ti film increased the hardness of the substrate. This is mainly due to the good bonding between the titanium layers and the higher microhardness. At the same time, the study also prepared AlOxNy/Ti and AlOxNy/Al films on the surface of AZ31 magnesium alloy. The results show that the surface hardness and elastic modulus of AlOxNy/Al are less than that of AlOxNy/Ti, which may be due to the soft Aluminum sandwich. This shows that titanium as an intermediate layer is superior to aluminum intermediate layer in terms of wear resistance.

In summary, the metal transition layer can effectively overcome the problem of mismatch between the composite coating and the magnesium alloy substrate; it can combine the composition of the film, reduce coating defects, increase the bonding strength between the film substrate, and greatly improve the composite corrosion and wear resistance of the coating. In the metal/ceramic composite coating, metal is used as the transition layer. In terms of corrosion resistance, the aluminum transition layer is better than the titanium transition layer; in terms of wear resistance, the titanium transition layer is better than the aluminum transition layer.

Table 2. Wear resistance of metal/ceramic composite coating on magnesium alloy

| Metal transition layer | Ceramic layer | Matrix material | membrane thickness/μm | hardness /MPa | Critical load/N | Coefficient of friction | references |
|------------------------|---------------|-----------------|------------------------|---------------|-----------------|------------------------|------------|
| Al                     | AlN/DLC       | AZ31            | 3                      | 3000 13600    | 0.36 0.10       | [5]                    |
| Al                     | TiAIN         | AZ91            | 5.15                   | 31300         |                 |                        | [11]       |
| Ti                     | TiN/TiC3N1-x  | AZ31            | 2.31                   | 17.9          |                 |                        | [8]        |
| Ti                     | TiN           | AZ31            |                        | 0.40 0.17     |                 | [14]                   |
| Cr                     | DLC           | AZ31            | 0.78                   | 7.7           | 0.40 0.30       | [15]                   |
2. The Influence of Process Parameters and Other Factors on the Corrosion and Wear Resistance of Metal/Ceramic Composite Coatings

There are few reports on the process parameters on the corrosion resistance of metal/ceramic composite coatings. Zhang Deqiu et al. [14] used magnetron sputtering to prepare Ti/TiN composite coatings on magnesium alloy substrates at different Ar/N2 flow ratios (11:2–11:5). The results showed that with the Ar/N2 flow rate with the increase of the ratio, the corrosion potential of magnesium alloy specimens has been improved. Among them, when the Ar/N2 flow ratio of the sample is 11:2, the degree of corrosion potential increase is most obvious, showing the best corrosion resistance. Guosong Wu [15] et al. analyzed the influence of different Cr concentrations (2.34~31.5at. %) on the corrosion resistance of Cr/DLC composite coatings by changing the flow ratio of Ar/CH4. The results of the experimental data show that the AZ31 of the Cr/DLC film with different Ar/CH4 flow ratios all exhibit a higher corrosion current density than the bare AZ31, which indicates that the Cr/DLC film cannot improve the corrosion resistance of the magnesium alloy. The reason is analyzed due to the formation of galvanic cell in the thickness defect of the magnesium alloy film.

In terms of wear resistance, Haitao Li et al. [8] explored the influence of different substrate negative biases on mechanical properties. As shown in Figure 1, with the increase of the bias voltage, the film-base bonding force and film thickness both show a trend of first increasing and then decreasing. When the bias voltage is 45V, the binding force and thickness of the film are the largest at this time. This is mainly due to the increase in the energy of the deposited particles as the bias voltage increases, so that the particles have a higher deposition rate and a stronger adsorption force. However, when the negative bias voltage exceeds 45V, the binding force and thickness tend to decrease. This is because the particle energy is too high, resulting in reverse sputtering, resulting in a decrease in film thickness; at the same time, high-energy particles will also cause the substrate temperature to rise, making the thermal stress between the film and the substrate increases, thereby reducing the bonding force. At the same time, the scholar also studied the influence of different sputtering currents (0.3, 0.35, 0.4, 0.45, 0.5) on film properties. The study found that as the current increases, the thickness of the film increases, but the binding force increases and then decreases. In addition, gas flow ratio is also an important parameter for coating performance. Deqiu Zhang et al. studied the effect of Ti/TiN composite film on wear resistance by changing the Ar/N2 flow ratio. As shown in Figure 2, the coating samples with different Ar/N2 flow ratios effectively reduce the friction work compared to the magnesium alloy matrix and improve the wear resistance of the magnesium alloy. Among them, when the flow ratio of Ar/N2 is 11:2, the friction coefficient is the lowest, the degree of bonding between the film and the substrate is the best, and its wear resistance is the best. In summary, an appropriate gas flow ratio helps to improve the corrosion and wear resistance of the metal/ceramic composite coating. Excessive bias voltage and sputtering current are not conducive to the combination of the composite coating and the substrate.

![Figure 1. Film base bonding force and film thickness of Ti/ TiN/TiCxN1-x films under different bias p-](image-url)

![Figure 2. The properties of Ti/TiN films at different Ar/N2 flow rates resurses](image-url)
The corrosion resistance of the metal/ceramic composite coating is not only related to the process parameters, but also to other factors, such as the number of layers, annealing treatment and other factors. Haitao Li [8] discussed the corrosion resistance of different annealing temperatures on AZ31 magnesium alloy magnetron sputtered Ti/TiN/TiCxN1-x composite coatings. As shown in Figure 3, as the annealing temperature increases, the film moves toward the direction of increasing electric potential and decreasing current density. Compared with the substrate, the corrosion resistance of the annealed film is improved, and the corrosion resistance of the film annealed at 300°C is the best. Dongfang Zhang [14] et al. used magnetron sputtering to deposit Hf/Si3N4 composite coatings with different alternating layers (n = 1, 2, 10, 20) on the surface of AZ91 magnesium alloy. As shown in Figure 4, the corrosion resistance of Hf/Si3N4 coating with different alternating layers is significantly improved compared with the magnesium alloy matrix. With the increase of the number of alternating layers, the Hf/Si3N4 coating gradually moved to the direction of low corrosion current density. However, when the number of layers is n=20, the corrosion current density rebounds. The main reason is that the refinement of the HF sub-layer leads to a significant negative impact on the grain boundary, which leads to a slight increase in porosity.

![Figure 3. Corrosion potential and corrosion hfsi3n4 current density at different annealing temperatures](image)

![Figure 4. Corrosion current density of coating at different layers](image)

3. Summary and Outlook
The surface of metal and metal/ceramic coating of magnesium alloy can improve the corrosion resistance and wear resistance of magnesium alloy. The Al layer of the transition layer in the metal/ceramic composite coating is better than the Ti layer in terms of corrosion resistance, and the Ti layer of the transition layer is better than the Al layer in terms of wear resistance. The disadvantage of metal/ceramic composite coating research is that the prepared coating has many structural defects, which affect its performance. Reducing the structural defects of metal/ceramic coatings will further improve the corrosion resistance and wear resistance of magnesium alloys. The structure and performance of metal/ceramic coatings are susceptible to the influence of metal transition layer, process parameters, post-processing and other factors. At present, there is still a lack of systematic research on influencing factors, and further research is needed.

The process parameters have a greater impact on the structure and performance of the coating. The longer the sputtering time, the thicker the film, but too long a sputtering time will result in a decrease in the bonding strength. The bonding force between the film and the substrate can be improved by changing the appropriate bias voltage. Properly increasing the temperature can improve the corrosion resistance of the film, but too high a temperature will cause the thickness of the film to decrease. At present, for magnesium alloy magnetron sputtering metal/ceramic composite coatings, there is still a lack of optimization of process parameters and the interaction mechanism between metal transition layer and ceramics. Therefore, for the preparation of metal/ceramic composite coatings, the process parameters should be reasonably optimized, and the deposition mechanism of the interaction between...
the metal layer and the ceramic layer should be studied in depth to effectively prepare the metal/ceramic composite coating with excellent performance.

With the rapid development of magnetron sputtering technology, the film prepared has a diversified structure and multiple excellent properties. Exploring the process system for preparing metal/ceramic composite coatings by magnetron sputtering and realizing the industrial production of composite films has engineering application significance and potential economic value.

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