

# Patent Analysis of Aluminum Based Sacrificial Anode Materials at Domestic and Abroad

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**Abstract:** Aluminum-based sacrificial anode is a new kind of sacrificial anode material developed rapidly in recent years. It has many advantages, such as low price, high potential of metal driving, large theoretical capacity and rich resource reserves, and is widely used in marine facilities and petroleum industry. However, the related contents of aluminum-based sacrificial anode are various and difficult to be analyzed statistically. On this basis, the relevant patents of aluminum-based sacrificial anode published at home and abroad are statistically analyzed. According to statistics, China's marine aluminum-based sacrificial anode material patent ratio is 73.4%, oil field aluminum-based sacrificial anode material patent ratio is 26.6% . Foreign patents on aluminum-based sacrificial anode have a long history, and the number of patents after 2000 is relatively small. In addition, according to the three categories of component design, preparation process and auxiliary device, the contents of relevant patents are statistically analyzed. It is found that in recent years, the number of patents related to aluminum-based sacrificial anode auxiliary device is higher than the other two types. In terms of the number of patents published, there has been a sharp increase since 2010, with more than half coming from corporate R & D. At the same time, by classifying the composition of aluminum alloy sacrificial anode material in the patent, the content of zinc, indium, tin, magnesium and titanium in aluminum-based sacrificial anode materials and their effects on the properties of anode materials are summarized, the application of alloying elements at home and abroad is compared and analyzed. The effects of zinc content and gallium content on the performance of anode materials were discussed. Finally, some suggestions on the development of aluminum-based sacrifice are put forward.

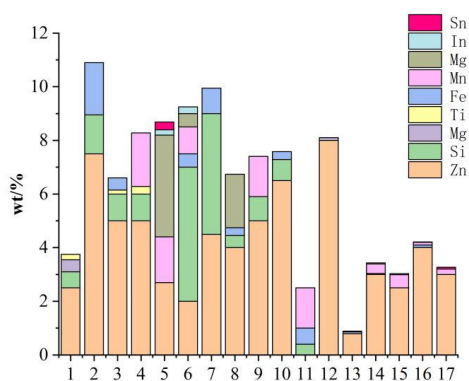
**Keywords:** Cathodic protection of sacrificial anode; alloy; patent analysis.

## 1. Introduction

Corrosion of metal materials is a very common phenomenon in production and daily life. It is caused by chemical or electrochemical interaction between metal and environment. Aluminum-based sacrificial anode material is the fastest developing type of sacrificial anode material in recent years. Aluminum-based sacrificial anode materials have the characteristics of wide distribution, high content, large theoretical capacitance and moderate driving potential. The main method to develop aluminum-based sacrificial anode materials is alloy method, that is, adding a few alloy elements into pure aluminum to destroy the formation of oxide film on aluminum surface and make aluminum-based sacrificial anode uniformly dissolve in the process of operation.

As shown in Figure 1, the category and content of non-aluminum metal elements in the patent of aluminum-based anode material outside China. As you can see from the diagram, there are many types of add elements. In addition to common elements such as zinc, indium and tin, the most common metal elements are iron, silicon and manganese. Because of the early aging of the sample, the addition of elements has little effect on the activation performance of the aluminum alloy anode. It is found that adding a small amount of silicon into the aluminum-based anode can refine the particles and improve the solubility of the anode. The increase of the number of the second phase in the anode leads to the increase of the precipitates in the grain boundary and the formation of a large number of cathodic phases, which leads to the preferential dissolution of the grain boundary, aggravates the tendency of self-corrosion of the anode and seriously affects the uniformity of the anodic dissolution, when the iron content is too high, not only the coupling current decreases, the coupling potential moves forward, the electrode process is hindered, and the activation of In is limited, thus the active dissolution resistance is gradually increased.

At present, the common ternary aluminum alloys are Al-Zn-In series, Al-Zn-Sn series and Al-Zn-Hg Series [5] . However, due to the harm of some metal elements to human health and environment or the influence of high production cost, al-zn-in series aluminum alloy materials are mainly developed in combination with actual production. With the increasing maturity of element proportion and production process, China promulgated the national standard of al-zn-in alloy sacrificial anode in 2002. Since then, the composition innovation of aluminum-based anode materials has become more and more mature, such as adding Cd, Sn, Si, Mg and other elements to form Quaternary or pentagonal alloy,



**Figure 1.** Schematic diagram of the content of metals other than aluminum in various foreign samples

further improving the performance of aluminum alloy anode materials. The data of this paper are from CNKI and American patent database. The deadline of data retrieval is August 31, 2022. Taking the patents under review as the original sample base, the sample base was carefully checked, and the irrelevant and weakly relevant patents were screened out. Finally, the number of texts in the sample base was calculated to be 126.

## 2. Classification of Patent Types

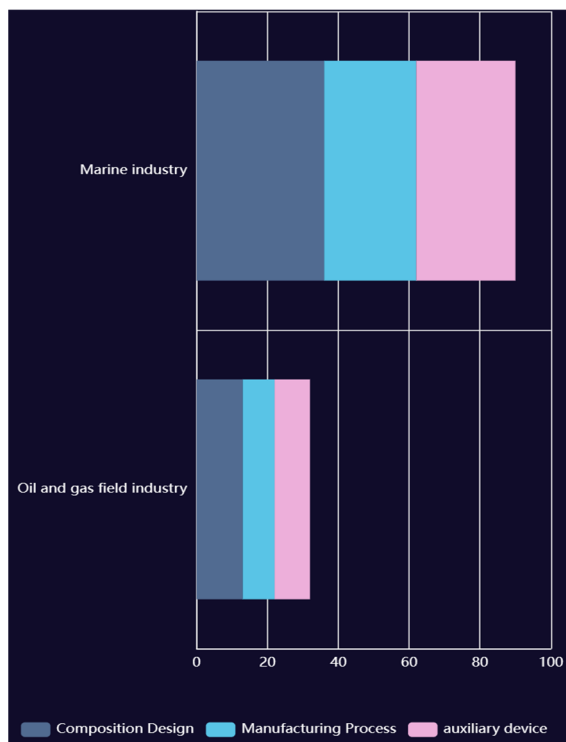


Figure 2. Classification proportion of domestic patent content

Based on the analysis of domestic sample data, it can be divided into two types: aluminum-based sacrificial anode for oil and gas field and aluminum-based sacrificial anode for ocean engineering. Of these, 73.4% were used for ocean engineering and 26.6% for oil fields. Further subdivided into three parts: component design, manufacturing process and auxiliary equipment. Among them, there are 28 kinds of auxiliary devices, 36 kinds of component designs and 26 kinds of manufacturing processes in the marine aluminum-based anode material patents, and 10 kinds of auxiliary devices and 9 kinds of manufacturing processes in the oil field patents, 13 component designs.

Seawater corrosion and oil and gas field corrosion face different situations due to different service environments. The Corrosion of seawater is mainly caused by the high concentration of chloride ion in seawater and the planktonic algae and bacteria. The corrosion conditions of metals in seawater are different at different depths. The corrosion areas from top to bottom are marine atmosphere, splash, tidal range, complete immersion and mud area [6]. With the decrease of the corrosion depth, the temperature of the corrosion environment also decreases. The surface of the anode material is adhered to by sediment and planktonic algae in seawater, and these factors will make the protection of the anode material lose efficacy, the protection of the anode material during installation must also be considered.

The corrosion environment of oil and gas field is very complex. There are a lot of  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{Cl}^-$  in the corrosion medium. At the same time, in the process of oil and gas production, equipment exposed to high temperature, high pressure, high flow corrosion environment. Anode materials in oil and gas fields are mainly used for anti-corrosion of oil and gas production equipment and oil and gas transmission pipeline. Because of the high content of chloride ion in the produced water, the temperature is about  $70^\circ\text{C}$  and the wear is serious, the corrosion rate of metal increases obviously. Therefore, the anode materials used in oil and gas fields should have both adequate wear resistance and high temperature resistance.

## 3. Analysis of Patent Related to Composition Design

In the patents related to composition design, other alloy elements are mainly added to aluminum to improve the performance of anode materials. According to the national standard for aluminum indium tin sacrificial anode materials issued by China in 2002, the main alloy elements added in China are mostly Zn, In, Sn, Mg, Ti, etc.

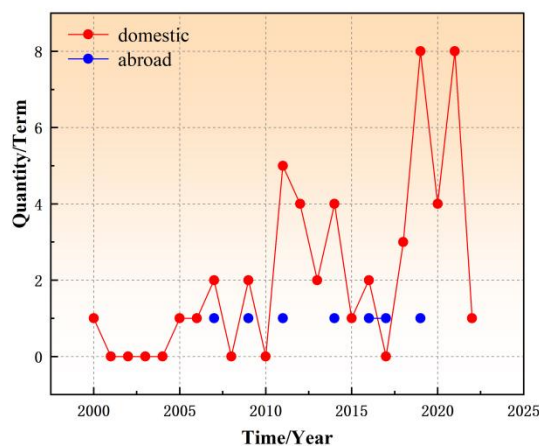


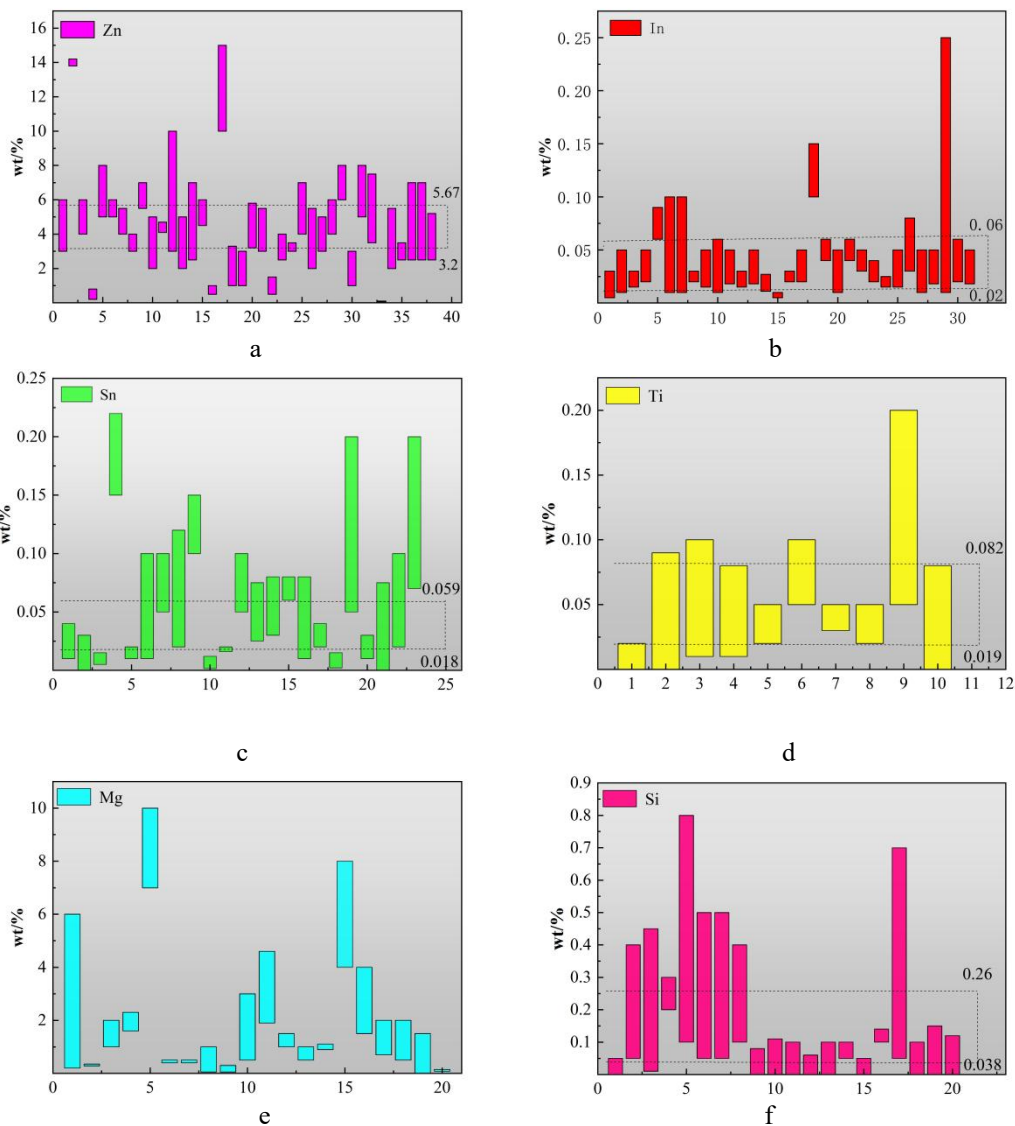
Figure 3. Trend of Patent Applications for Aluminum Based Sacrificial Anode Composition Design at Home and Abroad

The fifth plenary session of the 17th Central Committee of the Communist Party of China (CPC) adopted the outline of the 12th five-year plan for national economic and social development. Therefore, it can be seen from Figure 3 that after 2010, the number of domestic patents for the design of aluminum-based sacrificial anode material composition has increased significantly compared with the previous years, while the relevant foreign patents were published earlier due to the earlier time, the number after 2010 is relatively small.

With the rapid development of China's oil industry and the high attention to marine resources, oil drilling and offshore platform facilities are facing corrosion problems. Zinc, indium, tin, magnesium and titanium are important alloy elements in aluminum-based sacrificial anode materials. Zinc is the most basic alloy element in aluminum alloy sacrificial anode, its main role is to adjust the negative displacement of anode [7]. In addition, it can promote the aluminum alloy anode dissolution uniformity, easy alloying function, help to improve the solubility of aluminum alloy sacrificial anode. In the environment containing  $\text{Cl}^-$ , such as seawater, a small amount of In can significantly improve the activity of aluminum alloy, resulting in negative shift of anode potential

and improvement of current efficiency. With the increase of In content, the uniformity of the microstructure decreases, and the pitting becomes uneven, which leads to segregation and further aggregation, resulting in a large number of pitting corrosion, and finally leads to the local stripping of the anode and the formation of macro pitting corrosion, this leads to low capacitance and insufficient potential protection. The

electrochemical properties of aluminum alloy anodes can be significantly improved by appropriate amount of magnesium. The capacitance of sacrificial anode increases with the increase of MG content. The change of magnesium content can improve the electrochemical performance of sacrificial anode by affecting the particle size, amount and distribution of precipitates.



Figures 4. a, b, c, d, e, and f represent the content statistics of Zn, In, Sn, Ti, Mg, and Si in all samples, respectively

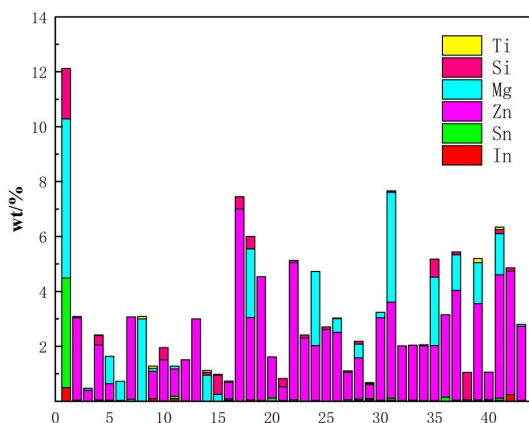


Figure 5. Schematic diagram of metal content other than aluminum in domestic patent samples

Figure 4 shows the application of the six major alloy elements in the aluminum-based sacrificial anode material.

As can be seen from the diagram, the contents of several alloying elements are generally in several constant ranges. Therefore, after excluding special phases, relevant data can be sifted and the limit of metal content can be calculated. The content of In and Sn were 0.02% ~ 0.06% and 0.018% ~ 0.059%, respectively. The distribution range of Mg content was wide, but most of Mg content was about 2%, it mainly exists in T phase (Al<sub>2</sub>Mg<sub>3</sub>Zn<sub>3</sub>)[8] and plays an active point role in promoting anodic dissolution. Zinc is the most important alloy element in ternary aluminum alloy. The content of zinc is mostly between 3.2% ~ 5.67%, the content of titanium is mostly between 0.019% ~ 0.032%, and the content of silicon is between 0.038% ~ 0.26%.

By comparing figure 5 and Figure 1, it can be seen that there are significant differences in the use of zinc at home and abroad. The domestic patent shows that the best addition of zinc is about 4%, while most of the foreign zinc elements are above 5%. Through a lot of experiments, it is found that zinc can reduce the stability of the oxide film on the surface of pure aluminum under the action of other elements. When the content of Zn is less than 5%, there is  $\alpha$  formation, which ensures a stable working voltage and good efficiency, and when the content of Zn is more than 5%, the formation and dispersion of phase have a core effect due to the action of  $\beta$ , causing severe mechanical losses, resulting in a significant decrease in efficiency. At the same time, from an economic point of view, too high zinc content is meaningless.

Iron and silicon are also frequently used in foreign patents, the amount of these two elements need to be strictly controlled. It was found that the number of active sites increased when the iron content was below 0.1%, resulting in a relatively negative and stable coupling potential. However, with the increase of the amount of iron, the anode itself corrodes seriously in the initial dissolution stage, resulting in grain shedding and the decrease of anode current efficiency. Similarly, when the silicon content is less than 0.09%, the grain size becomes smaller and more uniform with the increase of silicon content in aluminum alloy. However, with the increasing silicon content in the anode, the actual capacitance decreases and the current efficiency decreases. In China, with the continuous exploration in the field of aluminum-based sacrificial anode, several more valuable metal elements have been found, such as Mg and In. The results show that Al-Mg binary alloy is an important alloy without heat treatment, and the properties of some alloys can be changed according to the requirement. Adding proper amount of magnesium can not only improve the toughness of the alloy, but also weld it. The matching of magnesium and tin can improve the anode current efficiency significantly when there is a small amount of tin in the alloy. The formation of oxide film on aluminum alloy surface was destroyed by

enhancing the adsorption of chloride ion. In can also synergize with Zn to further improve the activity of the alloy. Although the amount of In is strictly controlled, the relevant standards show that 0.02% of In is the most suitable amount of Al-Zn In-based anode material, in element can also solve the problem of producing high silicon content from industrial pure aluminum.

Ga element is a kind of activated aluminum alloy with great research and development potential. It can change the anisotropy of aluminum particles during the dissolution process, thus achieving uniform corrosion of aluminum anode surface. The results show that the activation mechanism of gallium is due to its low melting point. Due to the deposition of low melting point metals with good mobility on the surface of aluminum alloy, a process similar to mercury reaction takes place, which destroys the dense oxide film on the surface of aluminum alloy and leads to the activation and dissolution of aluminum alloy. The activation of gallium on aluminum alloy is very significant, only a small amount of gallium can play a key role. Gallium can also cause significant negative shift of aluminum potential. It was found that the addition of 0.01% Ga could produce a negative shift of 0.3 V in the potential of aluminum, which was translated from LingoCloud.

#### 4. Summary and Suggestions on Technical Patents for Aluminum Based Sacrificial Anode Materials

In order to reflect the source of patent output more clearly, this paper classifies and counts the patent applicants and their affiliated organizations. As can be seen from Figure 6, among all sources of patent output, enterprises of various types accounted for 62.4%, scientific research units for 16%, universities for 15.2%, and individual ownership for 6.4%. Thus, with the aluminum alloy sacrificial anode related technology becoming more mature and practical, companies and enterprises in the sample source has accounted for more than 50%. The company's patents focus on practical problem solving and the design of practical auxiliary equipment, while other research institutes focus more on the type and proportion of material components to obtain different performance of sacrificial anode materials, or carries on the corresponding simulation experiment, namely simulates the sacrificial anode material protection in the different environment according to the concrete situation. Anode material is widely used in industrial production, which belongs to practical functional material. Therefore, in the invention patents owned by enterprises, more attention is paid to the difficulties of actual production and economic benefits, as well as can improve the material practical effect of the device and equipment.

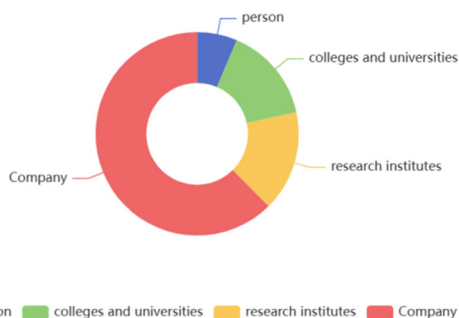


Figure 6. Analysis of the proportion of units to which the applicant belongs

## 5. Summary of Technical Patents for Aluminum Based Sacrificial Anode Materials

Based on the comprehensive analysis of the patents of aluminum-based sacrificial anode materials at home and abroad, aluminum-based sacrificial anode materials can be divided into oil and gas field uses and marine uses according to their application environment. In China, the basic proportion is 26.6% and 73.4% , which can be further divided into three categories: component design, manufacturing process and auxiliary equipment. In terms of the source and quantity of related patent output, more than half of the patents come from R & D, and since 2010, the total number of patents has exploded. In foreign countries, the ownership of technology patents in this field is relatively early, and the number of related patents will decrease in the future.

In the aspect of composition design innovation, aluminum-based sacrificial anode materials with different properties were obtained by adding different contents and types of alloy elements. In foreign patents, in addition to commonly used zinc, indium elements, but also added silicon, iron, manganese and other impurities, resulting in low production efficiency of anode materials. The common alloying elements in China are magnesium, tin, titanium and so on. The performance of the anode can be improved significantly by controlling the amount of zinc and gallium, and the efficiency of the anode can be improved by controlling the amount of zinc and gallium below 5% . In manufacturing process, most aluminum-based sacrificial anode materials are molded by casting. In order to improve the performance of al-based sacrificial anode material, various protective gases such as argon, nitrogen, refining agent and impurity remover can be added during the melting process. One part of the auxiliary device is the electrochemical test device which can optimize the function and simplify the operation, the other part is the auxiliary device which can improve the actual use effect of the anode material.

In terms of the units to which the patent applicants belong, the enterprise units accounted for the largest proportion, at 62.4% . It can be seen that the development of anode materials is more inclined to practical, enterprise R & D is also more inclined to auxiliary equipment. However, research institutions and universities prefer to study the composition and microstructure of innovation

## 6. Technical Development Suggestions for Aluminum Based Sacrificial Anode Materials

With the improvement of People's environmental awareness, the protection ability of metal components is getting higher and higher, and the performance of sacrificial anode material is required higher. At present, the development trend of aluminum alloy sacrificial anode materials includes the following aspects.

1) In the actual work process, there may be high temperature and high pressure oxygen system or gas-liquid-solid three-phase coexistence system, such as mixing, affect the performance of anode materials. Therefore, it is one of the main research directions to find a kind of anode material with high environmental friendliness and high performance.

2) Although the basic composition of aluminum-based sacrificial anode materials has been formulated specific standards, but further development of efficient, durable, economic and environment-friendly aluminum alloy sacrificial anode is still the future direction of development.

3) At present, the aluminum-based sacrificial anode performance test cycle is long, greatly delayed the large-scale production of the test efficiency. Therefore, it is important to study the fast performance test and evaluation technology of aluminum alloy sacrificial anode.

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