Available online www.jocpr.com

Journal of Chemical and Pharmaceutical Research, 2014, 6(1):346-350

Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Corrosion properties of ZrN films on the aluminium alloy surface prepared by magnetron sputtering process

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ABSTRACT

Aluminum alloy have the active chemical properties, low standard electrode potential, and the surface will be easily forming about 1-3nm oxide film in dry air, therefore aluminum alloy have the poor corrosion resistance. ZrN film deposited by mid frequency reactive magnetron sputtering process on aluminium alloy surface in order to improve the corrosion performance. Study the influences of nitrogen flow rate, sputtering time and temperature to the corrosion performance. The results show that: The corrosion performance of ZrN films will be improved with the nitrogen flow rate increase, but when the nitrogen flow rate was more than 18sccm, ZrN film corrosion resistance will be reduce. The corrosion performance improved with the sputtering time increase, when the time reach 15min, ZrN film corrosion resistance was no longer increase. The corrosion performance improved with the temperature, when the temperature reach 130℃, the corrosion resistance was no longer increase. The best process parameters was: nitrogen flow rate 18sccm, sputtering time 15min, temperature 130℃.

Key words: aluminum alloy; mid frequency magnetron sputtering; ZrN film; corrosion resistance

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INTRODUCTION

As we all know, aluminum alloy has high specific strength, good thermal and electrical conductivity, good reflection, good plastic, good formability, no low temperature brittleness. Aluminum alloy is an non-ferrous materials with excellent mechanical characteristic, which are widely used in modern automobile industry, aerospace industry, the electronic communications industry, computer industry and other fields. However, aluminum have the active chemical properties, low standard electrode potential, and the surface will be easily forming about 1-3nm oxide film in dry air, therefore aluminum alloy have the poor corrosion resistance. In order to overcome the shortcomings, expanding the applications range, improve the useful life of the aluminum alloy, the surface treatment process is very important which can solve or improve the corrosion resistance of aluminum alloy[1].

At present, the aluminum surface treatment process is widely used in electroplating, electroless plating, anodizing, powder coating and laser processing. This process not only pollute the environment, the process is complex, but also have the poor mechanical property which the film formed on the surface. Therefore, its have extensive research value and application prospect in strengthen the surface modification research of aluminum alloy, actively seeking a new surface treatment process research methods, reduce cost, reduce pollution, improve its application performance. Through the mid frequency magnetron sputtering process to deposit the ZrN films, which have the stable chemical structure, high corrosion resistance, good hardness and good wear resistance. If deposit the ZrN film on the aluminum alloy surface, it will significantly improve the corrosion resistance.

This research use the mid frequency magnetron sputtering process to deposit the ZrN film on the aluminum alloy surface, using optical profilometer to measure the film thickness, and use the YWX/Q-250 type salt spray device to do the corrosion resistance test in accordance with the national standard GB/T10125-1997.Optimize the process parameters of nitrogen flow rate, sputtering time and sputtering temperature, and get the best corrosion resistance of ZrN film[2,3].

EXPERIMENTAL SECTION

This experiment use 40×60mm,15×30mm aluminum alloy mirror panel as the deposition base which easy to do the corrosion resistance testing and measure the film thickness. Aluminum alloy mirror panels use the ultrasonic wave to clean, inject metal cleaning agent into cleaning agent, the temperature controlled at 50℃.After 10mins washing then use the ionized water to wash for 10 mins, and then use acetone wipe to dry, and finally with alcohol to blow dry. Do not use hands to contact the aluminum alloy mirror panel barely, which easy give rise to pollution in the panel surface and easy produce "fire" or "target poisoning" in the deposition process.

This experiment use SP-0707AS mid frequency magnetron sputtering machine to deposit the ZrN film on the aluminum alloy. This machine have the Φ700×700mm vacuum chamber, and the effective space was Φ500×500mm,which have the observation window can be observe the deposition situation real-time. Use the 270×70×5mm rectangular symmetrical Zr target, the purity of working gas Ar and reactive gas N_2 were 99.99%, divide two routes to control the flow rate of Ar and N_2 gas. The distance was 12cm between target and aluminum alloy, which can create a vacuum conditions better than 6.0×10^{-3}Pa vacuum. The sample frame was the 4 axis rotation system, which can realize step less speed regulation of the rotating frame through the frequency converter. Before the experiment, clean the vacuum room which satisfy with the requirements of deposition film.

The process for deposition ZrN thin film was: vacuum in the furnace, glow-discharge cleaning to the furnace and aluminum alloy sample, the main bombardment, deposition ZrN thin film, passive cooling, finally take out the sample. Other parameters were: sputtering power of 5KW,sputtering pressure 3×10^{-1} Pa, bias voltage 150 V, duty cycle 80%.

The specific testing process as follows:
(1)The nitrogen flow rate were:9, 12, 15, 18, 21, 24, 27 sccm, sputtering temperature 130℃, sputtering time 15min;
(2)The sputtering time were: 5, 10, 15, 20, 25, 30 min, nitrogen flow rate 18sccm, sputtering temperature 130℃;
(3)The sputtering temperature were: 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200℃, nitrogen flow rate 18sccm, sputtering time 15min;

TEST AND ANALYSIS

The influence of nitrogen flow rate to the ZrN film corrosion resistance

The nitrogen flow rate of this experiment process were: 9,12,15,18,21,24,27sccm,sputtering temperature 130 ℃,sputtering time 15min,all the sample number was 1-7.After the experiment, 1-7 sample do the corrosion resistance test which use YWX/Q-250 type salt spray device in accordance with the national standard GB/T10125-1997. The salt spray device parameters were: temperature 35 ℃,corrosive agent Ph=7 and 5%NaCl,spray pressure of 70～170KPa,salt spray deposition rate 1～2ml/h·80cm^2,sample surface and vertical surface placed by 30°,corrosion time 24h.The GB/T10125-1997 consists of 1 to 9 grade, 9 grade is the most excellent. The 9 grade is divided into 9.3 and 9.5 two super levels. Rate to 1-7 sample, the results as shown in Table 1, the corresponding diagram as shown in figure 1.

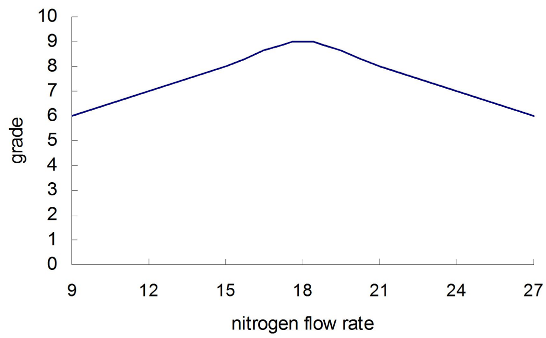

Fig .1 The relationship between nitrogen flow rate and corrosion

Tab.1 The influence of nitrogen flow rate to the ZrN film corrosion resistance

sample number	1	2	3	4	5	6	7
nitrogen flow rate(sccm)	9	12	15	18	21	24	27
corrosion grade GB/T10125-1997	6	7	8	9	8	7	7

From the table 1 results we can see that when the nitrogen flow rate reach 18sccm, the ZrN film corrosion resistance was best. With the increase of nitrogen flow rate, more and more nitrogen molecule connect with sputtering ion which form an compact and almost without any pore space ZrN film, therefore the corrosion resistance become better and better. As the nitrogen flow continues increase, the nitrogen reach the hypersaturated state in the vacuum furnace, nitrogen molecule and sputtering ion collision probability increases greatly, and have a serious collision scattering phenomena[4,5].Therefore reduce the particle energy which sputtering to the aluminum alloy surface, and reduce the gas molecule energy. These give rise to loose structure and form more pore space, which made corrosion resistance reduce.

The influence of sputtering time to the ZrN film corrosion resistance

The sputtering time of this experiment process were:5,10,15,20,25,30min,sputtering temperature 130 ℃ ,nitrogen flow rate 18sccm,all the sample number was 1-6. After the experiment, use optical profilometer to measure 1-6 sample film thickness and do the corrosion resistance test which use YWX/Q-250 type salt spray device in accordance with the national standard GB/T10125-1997.The results show that with the increase of sputtering time, the film thickness was increased, the film corrosion resistance was increased. But when time reach 15mins,the film corrosion resistance was not increased. The results as shown in Table 2, the corresponding diagram as shown in figure 2.

From the table 2 and figure 2 we can see that when the sputtering time reach 15min, the corrosion resistance reach the best. With the change of sputtering time, the film thickness was thin in the start time and exist much hole and defects.These will reduce the film corrosion resistance in the start time. But with the increase of sputtering time, more and more ZrN compounds produced, the film become more thick, which to cover the holes and defects[6-8].When the sputtering time reach 15min,it will form compact ZrN film and the corrosion resistance reach the best.

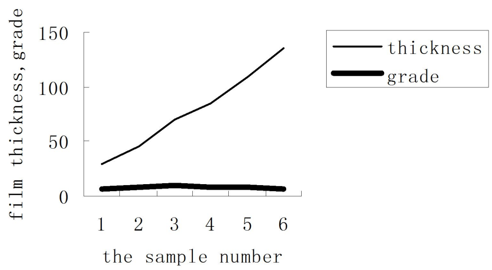

Fig .2 The relationship between sputtering time, film thin and

Tab.2 The influence of sputtering time to the ZrN film corrosion resistance

sample number	1	2	3	4	5	6
sputtering time(min)	5	10	15	20	25	30
film thickness(nm)	30	45	70	85	110	135
corrosion grade GB/T10125-1997	7	8	9	8	8	7

The influence of sputtering temperature to the ZrN film corrosion resistance

The sputtering temperature of this experiment process were: 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200℃,sputtering time 15 min, nitrogen flow rate 18sccm,all the sample number was 1-16.After the experiment,1-16 sample do the corrosion resistance test which use YWX/Q-250 type salt spray device in accordance with the national standard GB/T10125-1997,the results as shown in figure 3.

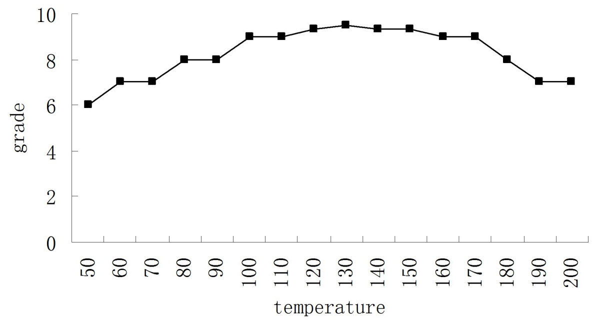

Fig 3 The relationship between sputtering temperature and corrosion

From the we can see that when the temperature reach 130℃,the corrosion resistance reach the best. When the sputtering temperature was low, the Zr ions and N ions energy was small, which can not fully diffused. This result in Zr ions and N ions connection probability was low and sputtering a small number of ZrN compounds on the aluminum surface, therefore appear more holes and defects. With the increase of temperature, Zr ions and N ions gained enough energy, more and more ZrN compounds was deposited on the aluminum alloy surface, which increase the corrosion resistance[9,10].When the temperature was more than 150℃,the high temperature will increase the thermal stress, lead to grain become big in the film structure, and reduce the corrosion resistance.

CONCLUSION

The ZrN film corrosion resistance increased with the nitrogen flow rate increase, when the nitrogen flow rate reach 18sccm, the ZrN film corrosion resistance reach the best. With the nitrogen flow rate increase, more and more nitrogen molecule connect with sputtering ion which form an compact and almost without any pore space ZrN film, therefore the corrosion resistance become better and better. As the nitrogen flow continues to increase, nitrogen molecule and sputtering ion collision probability increases greatly, and have a serious collision scattering phenomena. Therefore reduce the particle energy which sputtering to the aluminum alloy surface, and reduce the gas molecule energy. These give rise to loose structure and form more pore space, which made corrosion resistance reduce.

With the increasing of sputtering time, the ZrN film corrosion resistance increased first and then reduced. when the sputtering time reach 15min,the corrosion resistance reach the best. In the start time of deposition, the film thickness was thin and exist much hole and defects. These will reduce the film corrosion resistance. But with the increase of sputtering time, the film become more thick, which to cover the holes and defects. The corrosion resistance was increased gradually.

With the increasing of sputtering temperature, the ZrN film corrosion resistance was increased gradually. When the temperature reach 130℃,the corrosion resistance reach the best. When the sputtering temperature was low, the Zr ions and N ions energy was small, Zr ions and N ions connection probability was low and sputtering ZrN compounds number was small, which reduce the film corrosion resistance With the temperature increase, more and more ZrN compounds was deposited on the aluminum alloy surface, which increase the corrosion resistance.

Through the experiment, it obtained the best process of sputtering ZrN film on the aluminum alloy surface. It not only provides experience and technology to improve corrosion resistance of aluminum alloy parts and aluminum alloy products, but also provides a process and method for other poor corrosion resistance material, and has a broad theoretical research value and application value.

Acknowledgements
This research work was supported by the Foundation of the undergraduate education innovative highlands construction projects of Hebei Province-The agricultural mechanization education innovative highlands.

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