The Preparation Method of Aluminum-magnesium Alloys

Shan-Shan ZHU, Hong-Min KAN*, Xiao-Jun FENG, Ning ZHANG and Hong SUN

Key Laboratory of Advanced Materials Technology of Liaoning Province, Shenyang University, Shenyang

*email:kanhongmin2002@163.com

email:893341108@qq.com

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Abstract. In this paper, the preparation methods of aluminum-magnesium alloys are reviewed. The three methods of preparation of aluminum-magnesium alloys are introduced: the mixing method, mechanical alloying method, electrodeposition method. And the advantages and disadvantages and characteristics of three methods are expounded. Nowdays, the mixing method and mechanical alloying method are relatively mature. But heat consumption is great. Compared with mechanical alloying method, the electrodeposition method requires simple equipment and it's easy to operate. More uniform grain can be obtained. It has attracted general concern to prepare Al-Mg alloys by the electrodeposition method. In this paper aluminum-magnesium alloys are prepared by direct current electrodeposition and pulse electrodeposition in $AlCl_3$-$LiAlH_4$-benzene-tetrahydrofuran (THF) system. The deposit morphology and chemical compositions of coatings by direct current and pulse electrodeposition are compared. The effects of the pulse duration ratio on coatings are studied. The coatings obtained by pulse electrodeposition are greater than the coatings obtained by direct current electrodeposition under the same electroplating conditions. The grain sizes of the coatings obtained by pulse electrodeposition are smaller, and the magnesium contents of the coatings are higher.

Introduction

Aluminum-magnesium alloys have low mass, non-toxic, strong corrosion resistance and good machinability, etc. It is widely used in aviation, automobile, architecture and daily life[1-2]. Many researchers continually seek for the methods of preparation of magnesium-aluminum coating because of its decorative, strong oxidation resistance and excellent mechanical properties. The theoretical amount of magnesium hydrogen storage can reach to 1000mAh / g. And the resource of magnesium alloys is rich and the cost of magnesium alloys is low [3]. Aluminum-magnesium alloys are regarded as one of the most potential hydrogen storage material, which received extensive attention of worldwide specialists.

Nowdays, there are many ways to preparation of aluminum-magnesium alloys, such as, electrical deposition method, mechanical alloying method, the mixing method, molten salt electrolysis method, melting method, powder sintering, electron beam evaporation, magnetron sputtering, hydriding combustion synthesis method, diffusion method, etc[4-5]. Aluminum-magnesium alloys prepared by mechanical alloying have uniform and weenie structure. But long milling time is required. And it is easy to cause oxidation and to be influenced by impurity elements. And the cost is high in the preparation. The mixing method will make magnesium lost because of secondary remelting. The craft process is complicated and needs longer time. Furthermore, the cost is also high. The process engineering is simplified by molten salt electrolysis method. This method is continuity in production, easy to control and without secondary burning of metal, low cost[6]. Compared with these methods, electrodeposition method is simple in operation. The quality of coating is high and deposition temperature is low. The dense magnesium-aluminum coating whose thickness is several hundreds of micrometers even natometre level can be prepared by adjusting the deposition parameters and can be used in shape complex parts [7].

The Mixing Method

The mixing method is the major ways of preparation of Al-Mg alloys. The quantity of magnesium added needs to be calculated in this method. Aluminum ingot is melted, then joins preheated magnesium ingot in the preparation. Al-Mg alloys can be produced after subsequent processing. Other magnesium alloys are also prepared by the mixing method. For examples, Xu Songbing prepared Mg-Sr alloys by the mixed method. The degree of Sr loss is very serious in the preparation process. Even intense combustion will occur if no protection measures is adpotted[8]. The mixing method is also used in the preparation of certain aluminum alloys. For example, Song Dongming successfully prepare Al-10% RE master alloys using the mixed method[9]. The biggest advantage of this method is simple to principle and simple to operation. And the devices are easy to configure. The process flow is short. The composition can be controlled precisely. It won’t produce any harmful "three wastes" during the production. But faults are just as patent. The secondary remelting heat consumption not only increases by using this method, but also increases oxidation loss of metal. The recovery rate is low. The oxidation loss of magnesium will be greater because of the living chemical nature of magnesium. These defects will lead to high production cost of Al-Mg alloys, reduce commercial and industrial value. And the protective gas in the manufacturing process does great harm to the human body [10].

Mechanical Alloying Method

Mechanical alloying method is implemented under solid state, no gaseous phase and liquid phase, and it’s not constrained by material melting point, vapor pressure and other physical factors. It was difficult to achieve alloying stances in the past and some new substances keeping away from nonequilibrium state of thermodynamic equilibrium, quasi-steady-state. The mechanical alloying method makes it possible. Zaluski prepared Mg-Ni alloys whose grain size is 25nm using mechanical alloying method [11]. Ivanov prepared Ni-Al system alloys by the method of mechanical alloying [12].

A large amount of research results have shown that the aluminum-magnesium alloys produced by mechanical alloying method has high-activity and large capacity. This method become attractive preparation method of Al-Mg alloys hydrogen storage material. Hydrogen storage properties of alloys are greatly increased [13]. Al-Mg alloys prepared by mechanical alloying method have many advantages, for example: Firstly, the operations are relatively simple, and the cost is low. Secondly, operational program is continuous and adjustable and grain size is small. Thirdly, the microstructure and composition of synthetic material can be controlled; people can prepare the nano-alloys in this way [14]. There are also some shortcomings of this method, for example, it requires long time to obtain nano-alloys, it is difficult to achieve large scale production, and the grain size is not uniform. The impurities introduced in the process of alloying make the materials properties be affected. At the some time, there are some shortcomings of aluminum -magnesium alloys prepared by mechanical alloying. For examples: first of all, various metal elements must be obtained from their respective metallurgical process before the production of alloys. The problems and shortcomings in metallurgical process of various alloys are included. Taking magnesium for instance, Pidgeon process mainly was adopts to smelt magnesium in our country. The Pidgeon process has got great development because of its small furnace, small investment, no electricity, low technical difficulty and low limitation from the environment and resources. But there are still many problems of Chinese Pidgeon technology, such as: high production cost, long process, high energy-consuming, serious environmental pollution, and so on. Beside, the corrosion resistance of magnesium is low. A dense oxidized film cannot be formed to isolate the reaction with oxygen at high temperatures. Therefore, good protection measures must be taken in the melting process. The SF6 in the shielding gas is released. It will cause serious threat to the environment [15].

Therefore, it needs complex equipment and difficult to operate, scale production is difficult. Simultaneously, production cycle is long, the grain size of the alloys obtained is uniform, and impurities are easy to be introduced in the preparation process and could affect its performance. If hydrogen storage capacity of alloys surpasses 3.0%, the preparation temperature must be 300 ℃. In addition, melting protection gas will also bring a series of environmental problems. There is no a satisfactory theoretical model to describe the process, and most technologies and reaction system of this method at the stage of test and developing [16].

Electrodeposition Method

Electrodeposition technology is a common preparation technology of alloys in recent years. Grain size can be controlled by adjusting technological conditions. People have successfully prepared a variety of nano-alloys using this technology. Fereshteh Ebrahimi professor from Florida University pointed out: Al - Mg nanocrystalline powers can be prepared by electrodeposition method. $Mg(AlH_4)_2$ metal hydrides are compound directly by the reaction of this powers and hydrogen. These theories opened up new ideas for direct preparation $Mg(AlH_4)_2$ metal hydride ligand and illustrated that the component of aluminum-magnesium nano-phase alloys have a greater impact on the mechanism of absorption and desorption of hydrogen[17].

According to the difference of current types, the electrodeposition method is divided into direct current deposition method and pulse electrodeposition method. DC deposition method is traditional electrodeposition method of aluminium. With the improvement of life quality, pulse electrodeposition technology emerges [18].

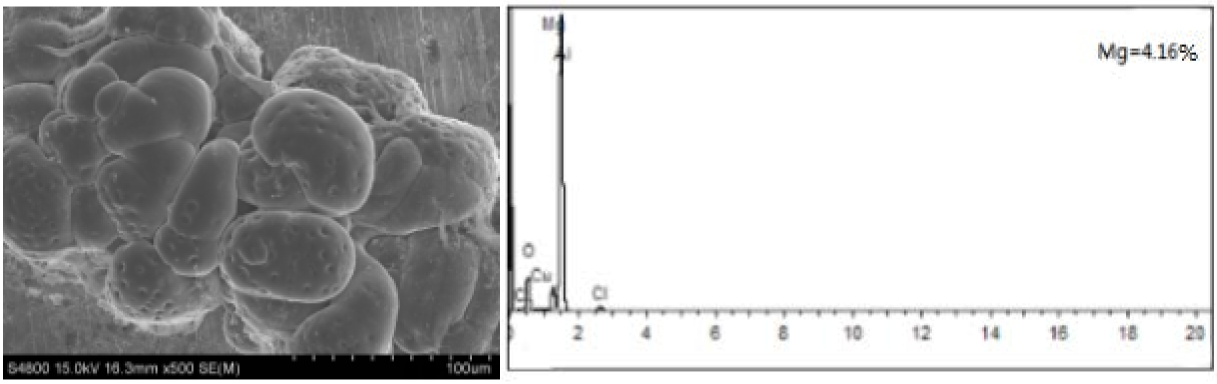
In the early study of electrodeposition, direct deposition method was widely adopted. The advantages are: the equipments are simple; this method is easy to operate. Disadvantages are: concentration polarization and hydrogen evolution reaction are easy to produc and affect the quality of the plating layer. If the current is too large, it may also cause "scorch" phenomenon in plating. Under the same conditions, the average current density of pulse electrodeposition is lower than the limitation of DC deposition, amounting to 70% ~ 100% of DC deposition. Aluminum coating prepared by pulse electrodeposition has smaller grain size, the surface morphology is more uniform and dense, physical and chemical properties is more superior[19-20]. Zhang and others studied that the abrasive resistance of coating are affected through pulse parameters. They pointed that coating obtained by the pulse electrodeposition method has low porosity and good wear resistance by measuring the porosity of the pulse plating, current efficiency and polarization curves [21].

At present, Al-Mg alloys prepared by pulse electrodeposition method have been paid more attention. But it's still in its infancy. There is few research results about this method [22]. P.Fellner and others researche pulse current in $AlCl_3$-NaCl-KCl molten salt system and found that the pulse current density was higher than DC current density. The current density is from 15 A/dm^2 to18 A/dm^2. Li Bing, et al, succeeded in preparing aluminum at $AlCl_3$-EMIC ionic liquids by using the electrodeposition method and studied its properties. Experiment showed that the surface of aluminum coating which prepared by using the pulse electrodeposition method is smooth, dense and uniform than DC deposition method. Pulse temperature and current frequency have a great influence on the morphology of the coating. When the scope of the temperature is from 20°C to 90 ℃and the current density is in the range from 5 to 20mA / cm^2, concentration gradient of reactant decreases, and ion diffusion rate reduces, the coating thickness increases with the increasing of current density. When the temperature is at 60°C, the morphology is the best, porosity is the lowest and density is the highest. When the temperature is at 25°C, t_{on} = 80 ms, t_{off} = 20 ms, current density is at 8 mA/cm^2, the grain size obtained is the smallest [23]. If aluminium alloys are prepared by pulse electrodeposition, the coating surface morphology, grain size and thickness could be contrlled by pulse parameters, such as current density and over-voltage. Grain size would be reduced by improving current density and increasing over-voltage to obtain the nano-scale aluminum alloys coating [24].

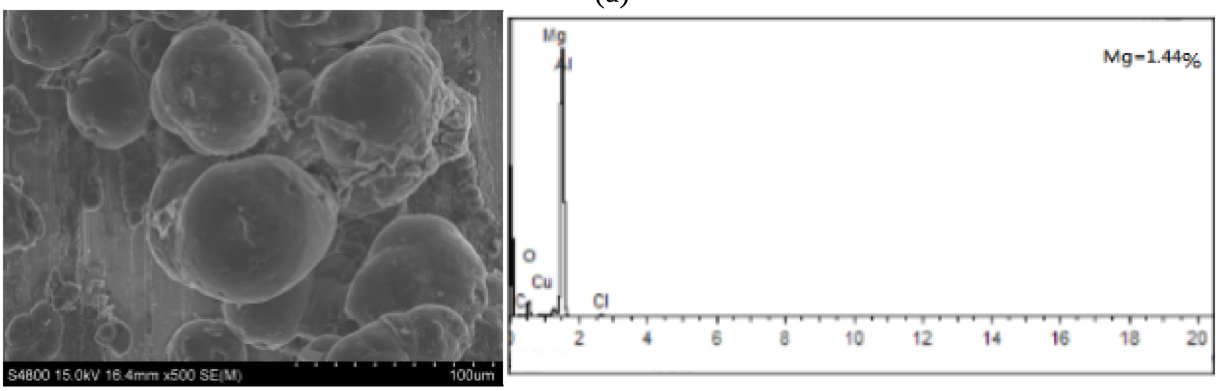
$AlCl_3$-$LiAlH_4$ system was one of the commonly used organic solvent systems. Aluminum-magnesium alloy coatings were prepared by direct current electrodeposition and pulse electrodeposition in $AlCl_3$-$LiAlH_4$-benzene-tetrahydrofuran (THF) system in this paper. The Mg^{2+}

ions were introduced into electrolyte by using two methods in the meantime. One way is to preliminary electroplating the magnesium rod which was used as the anode, and the other way is adding $MgCl_2$ into electrolyte. The whole experiments were conducted under a nitrogen atmosphere because aluminum and magnesium are active metals. The metals and oxygen or water from air can react to form oxide. The reacts can be effectively avoided in the inert gas. The aluminum-magnesium alloy coatings were tested by scanning electron microscope (S4800), and the chemical compositions were monitored using energy dispersive spectroscopy (EDS).

After preliminary electroplating, the pulse electrodeposition experiments were conducted under room temperature. The current density of pulse electrodeposition is 8 mA/cm^2, the duration ratio (t_{on}:t_{off}) is 0.08s:0.02s, frequency is 1000HZ for one hour. The SEM and EDS pictures of the coatings are shown in Fig.1a. The magnesium content of aluminum-magnesium alloys is 4.16%. The direct current electrodeposition experiments are carried under the same preliminary electroplating conditions. The current density of direct current electrodeposition is $8mA/cm^2$. The SEM and EDS pictures of the coatings are shown in Fig.1b. The magnesium content of coating is 1.44%. It can be seen from SEM pictures, the grain sizes of the coatings obtained by the direct current electrodeposition are huge, and grain sizes of the coatings obtained by pulse electrodeposition are relatively small.



(a)



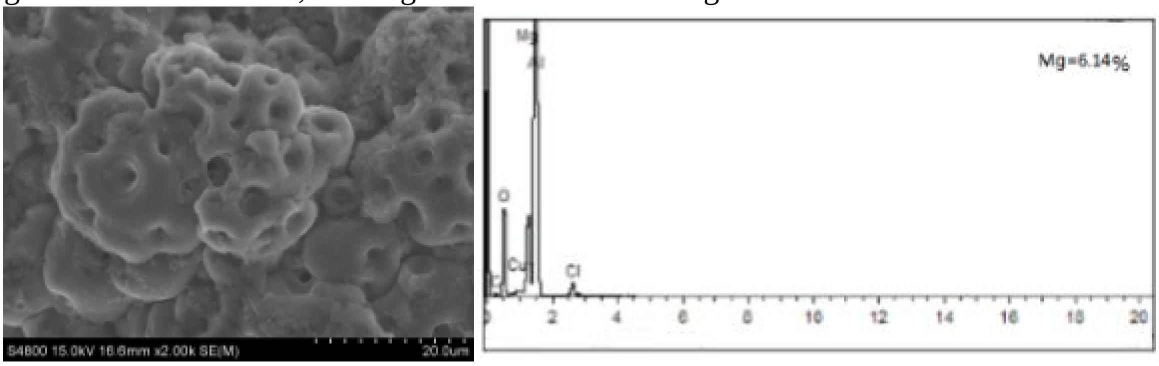
(b)

Fig.1 The SEM and EDS pictures of aluminum-magnesium alloy coatings (t_{on}:t_{off}=0.08s:0.02s)

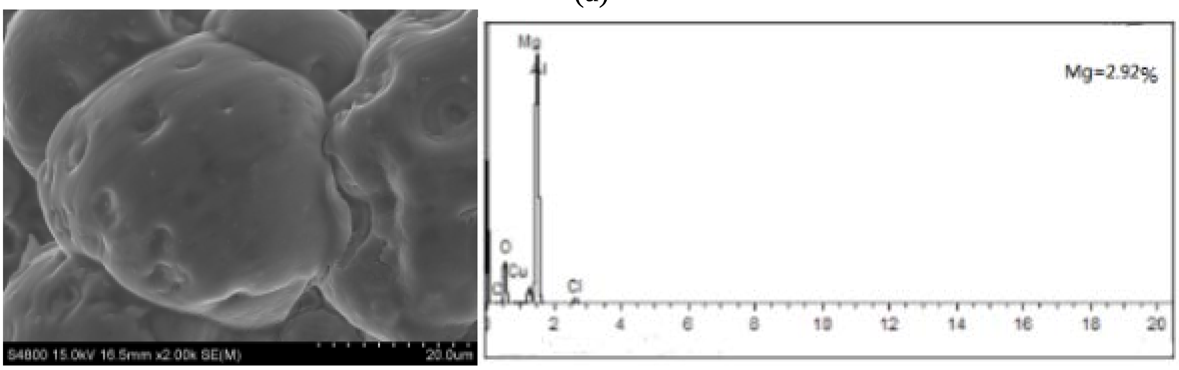
(a)pulse electrodeposition (b)direct current electrodeposition

The effects of the pulse duration ratio on the deposit morphology and chemical compositions of coatings are studied under different preliminary electroplating conditions. Fig.2a showed the SEM and EDS pictures of the coatings obtained by pulse electrodeposition at room temperature. The pulse experimental conditions are controlled to $i=8mA/cm^2$, t_{on}:t_{off}=0.02s:0.08s, f=1000HZ for one hour. The results showed that the magnesium content of aluminum-magnesium alloy is 6.14%. Fig.2b showed the SEM and EDS pictures of coatings by direct current electrodeposition under same preliminary electroplating conditions. The current density of direct current electrodeposition is 8 mA/cm^2. The magnesium content of obtained coating is 2.92%. And the grain sizes by direct current electrodeposition are greater than that of the coatings by pulse electrodeposition.

In conclusion, the magnesium contents are enhanced, and the grains are refined when pulse duration ratio is changed in pulse electrodeposition process. At same preliminary electroplating conditions, the magnesium content of aluminum-magnesium alloys by pulse electrodeposition are much greater than direct current electrodeposition. This is due to direct current deposition method can only change current parameter. Concentration polarization is easy to produce during the reaction. It is harmful to aluminum magnesium coatings. There are three alterable parameters in the pulse electrodeposition method. Deposition conditions are wider, the coating is more superior, the grains sizes are weenie, the magnesium contents are higher.



(a)



(b)

Fig.2 The SEM and EDS pictures of aluminum-magnesium alloy coatings (t_{on}:t_{off}=0.02s:0.08s)
(a)pulse electrodeposition (b)direct current electrodeposition

Conclusion

Nowdays, there are many ways of preparation of Al-Mg alloys. The mixing method and mechanical alloying method are relatively mature. But the mixing method not only increases the secondary remelting heat consumption, but also increases the metal oxidation loss, the recovery rate is low. The oxidation loss of magnesium will be greater because of the living chemical nature of magnesium. There are many disadvantages of mechanical alloying method, for example, good protection measures must be taken during the process of smelting, but the SF6 from shielding gas will cause great threat to the environment and high energy will be consumed during the experimental process and so on. Impurities are easy to be introduced by the mixing method and mechanical alloying method. However, the Al-Mg alloys was prepared by electrodeposition has high purity and uniform quality. Aluminum-magnesium alloy coatings were prepared by direct current electrodeposition and pulse electrodeposition in $AlCl_3$-$LiAlH_4$-benzene-tetrahydrofuran (THF) system in this paper. Under the same electroplating conditions, the more parameters can be changed in pulse electrodeposition, the coatings are more superior, the grain sizes are weenie, the magnesium contents in aluminum-magnesium alloy coatings are higher. It would be a new breakthrough of exploring nanometer alloys if nano-alumium magnesium alloys could be prepared successfully by the pulse electrodeposition method. Compared with aluminum-magnesium alloys, the morphology of nano-aluminum magnesium alloys coating are dense and uniformity, it has excellent performance, which can be used in the new weapons and space technology field.

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