Electroless Ni-P-TiO_2/Ni-P-SiC Composite Coating's Corrosion Resistances on $Mg_2B_2O_5$w/AZ91D Magnesium Matrix Composites

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Abstract. Ni-P, Ni-P-TiO_2 and Ni-P-SiC composite coatings on AZ91D magnesium matrix composite were prepared by the electroless composite depositing. The surface morphology of the coatings was observed by scanning electronic microscopy(SEM) and electron probe X-ray microanalyser(EPMA). The corrosion resistance of coatings were studied by the electrochemical method and the impact of TiO_2 and SiC was analyzed. The results showed that nano-TiO_2 and nano-SiC particles refining the depositing, cause the depositing loose, the corrosion resistance of composite depositing reduced. The corrosion potential is over -0.8V when 2g/L TiO_2 or SiC is added in solution, though the potentials lower than Ni-P coating(lower -0.5V), it still shows a protective effect for magnesium matrix composite.

Introduction

Since 1967, composite materials with its high specific modulus and strength, anisotropy, good fatigue resistance, easy molding and a large area can be given a new function, etc., are widely used in industry, sports, especially is concerned in aerospace in weight and performance demanding. Composite materials has made important contributions for improving aircraft performance, which has become one of the four major aerospace materials. Meanwhile, the rapid development of aerospace also accelerate the development of composite materials.

As another promising light metal matrix composites following the aluminum matrix composites, magnesium matrix composites related theories research has also been considerable development [1-3], but its poor corrosion resistance of magnesium matrix composites as a bottleneck which constraint to further development. Currently, the protection methods research is less on a magnesium-based composite material. Wang Xiaomin, etc.[4] has tried electroless Nickel plating on the surface of magnesium matrix composite material and has found that the plating played a protective effect to some extent. With the magnesium matrix composites being applied increasingly, the single Ni-P plating protection has cannot meet the high requirements of occasions gradually. Ni-P-SiC/Ni-P-TiO_2 composite coating could increase the wear resistance of materials greatly, but the corrosion resistance of composite coatings are reported rarely on the surface of the composite material. In this paper, the magnesium matrix composite as matrix, the Ni-P-SiC and Ni-P-TiO_2 composite coatings are prepared on the matrix, and the corrosion resistance effect of SiC or TiO_2 content of the coating are researched .

Experimental procedures

Preparation Material

The magnesium borate whisker reinforced AZ91D magnesium matrix composites (whisker volume fraction of 10%) are prepared by the method of vacuum pressure percolation[3]. Magnesium alloy chemical composition as shown in Table 1.

Table 1 Chemical composition of magnesium alloy AZ91D（wt，%）

Al	Mn	Ni	Cu	Zn	Ca	Si	K	Fe	Mg
9.1	0.17	0.001	0.001	0.64	<0.01	<0.01	<0.01	<0.001	Bal

Put the whiskers precast blocks(has been handled well) and AZ91D magnesium alloy in a mold of vacuum pressure flow furnace, vacuum, until the temperature rises to 720℃ and heat preservation 10min, after that, turning off the vacuum pump and increasing pressure, then the molten magnesium alloy infiltrated into the whiskers, keeping up the pressure 30min. After that, the material is cooled to the room temperature under a certain pressure. The mold is taken from the vacuum oven, drained away the mold, the magnesium matrix composites are prepared. Cut into 10mm × 10mm × 10mm in size.

Nickel plating solution

The formulations and processes of electroless nickel plating solution using magnesium-based composite material is researched by ourselves [4], the basic ingredients are as follows:

Table 2 compositions of nickel plating solution

$2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$	20g/L
HF	10 ml/L
$C_6H_6O_7$	5 g/L
NH_4HF_2	10 g/L
$NaH_2PO_2 \cdot H_2O$	20 g/L
NH_4OH	30 ml/L
PH	6.0-6.5
temperature	60-65℃
time	2h

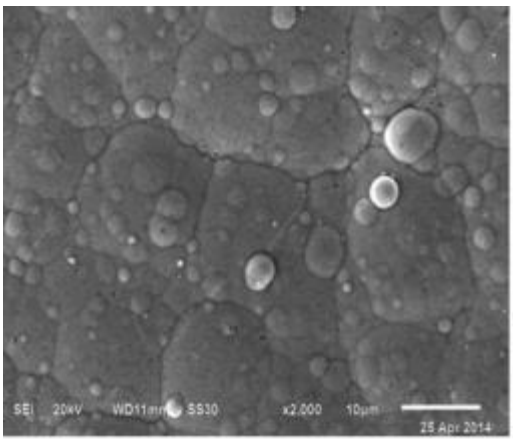

Figure 1 surface morphology of coating (SiC 2g/L)

On this basis, adding different concentrations nano-SiC (2g/L, 5g/L, 10g/L) or nano-TiO_2 (2g/L) in the bath. The process conditions remain unchanged. The sizes of nano-SiC and nano-TiO_2 are both less than 800 nm and the purity are greater than 99.9%.

Research Methods

For convenient electroless plating and the coating does not be affected when electrochemical testing, the samples must be produced by an electrode before the composite plating Ni-P-SiC or Ni-P-TiO_2. One end of the sample is exposed to the etching solution, and the other end connected with a wire, solid sealing with epoxy resin around and area which exposed to the solution is about 1 cm^2. Sample easy hanging in the bath, in favor of a uniform distribution of the coating SiC or TiO_2 particles.

Process: polished→degreasing→pickling→activation→plating→dry, washed with distilled water between each step. Magnesium-based composite material should be pretreated prior to plating strict: (1) Degreasing: A sample was immersed in an acetone solution and ultrasonic cleaning 15min,

to remove grease and dirt of the composite material surface; (2) Pickling: hydrofluoric acid (10% Vol) for sample 2-3min, removing the oxide film surface of the material, instead of using a solution of chromic acid or chromate which pollution of the environment; (3) activation: the sample was immersed in 3-5%(weight) solution of sulfuric acid, about 10s (surface bubbles evenly). Then the sample must immersed in the plating bath immediately.

Electrochemical measurement: The corrosion medium is formulated with NaCl (AR) and distilled water (w(NaCl) = 3.5%). Standard three-electrode electrochemical test system is adopted: Coating as the working electrode, saturated calomel electrode (SCE) as reference electrode, a platinum sheet as auxiliary electrode. Test condition is room temperature.

Test characterization

(1) Corrosion morphology The EVO MA 10/LS 10 scanning electron microscope (SEM) is used to observe the surface morphology of the coating before and after corrosion.

(2) Electrochemical performance The CS2350 dual-channel electrochemical workstation is used to test the open circuit potential-time (E-t) curves, polarization curves and electrochemical impedance curve. Ni-P/Ni-P-SiC/Ni-P-TiO_2 coating samples as the working electrode (sealed with an organic glue, exposed test area of 1 cm^2), saturated calomel electrode as the reference electrode, a large area platinum sheets as auxiliary electrode. Corrosion media is 3.5%(weight) NaCl solution, adjusting the pH value of 7.0 with a lightweight magnesium. The polarization curves scanning range is -1V-+1V, scanning rate is 0.5 mV/s. AC impedance test frequency range is 0.1Hz-100KHz.

(3)Binding Coating adhesion is measured by thermal shock experiments and file experiments. File experiments: File and the coating surface is 45º, exposing the substrate and coating interface, observing the coating whether peeling or shedding. Thermal shock experiments: The sample is placed in an incubator for 30min at 200 ℃, then put into the cold water, repeated tests, the coating was observed whether cracking or peeling.

Results and Discussion

Coating surface morphology

Because of the specific surface area and the surface energy are large, nanoparticles are easy to aggregate in solution. But the fluoride in the bath reduces the agglomeration of nano SiC or TiO_2 particles effectively[5], combined with constant mechanical stirring, particle distribution's composite coating is obtained. The plating surface morphology of magnesium matrix composites in different concentration SiC or TiO_2 in the plating bath are shown in Fig. 1. a) pure Ni-P coating, as a comparative experiment, denoted by 0 g/L.

Compared with pure Ni-P coating(Fig.1 a), the composite coating surface grain are finer and uniform when adding SiC (Fig. 1 b)or TiO_2 (Fig. 1 e) nano-particles.

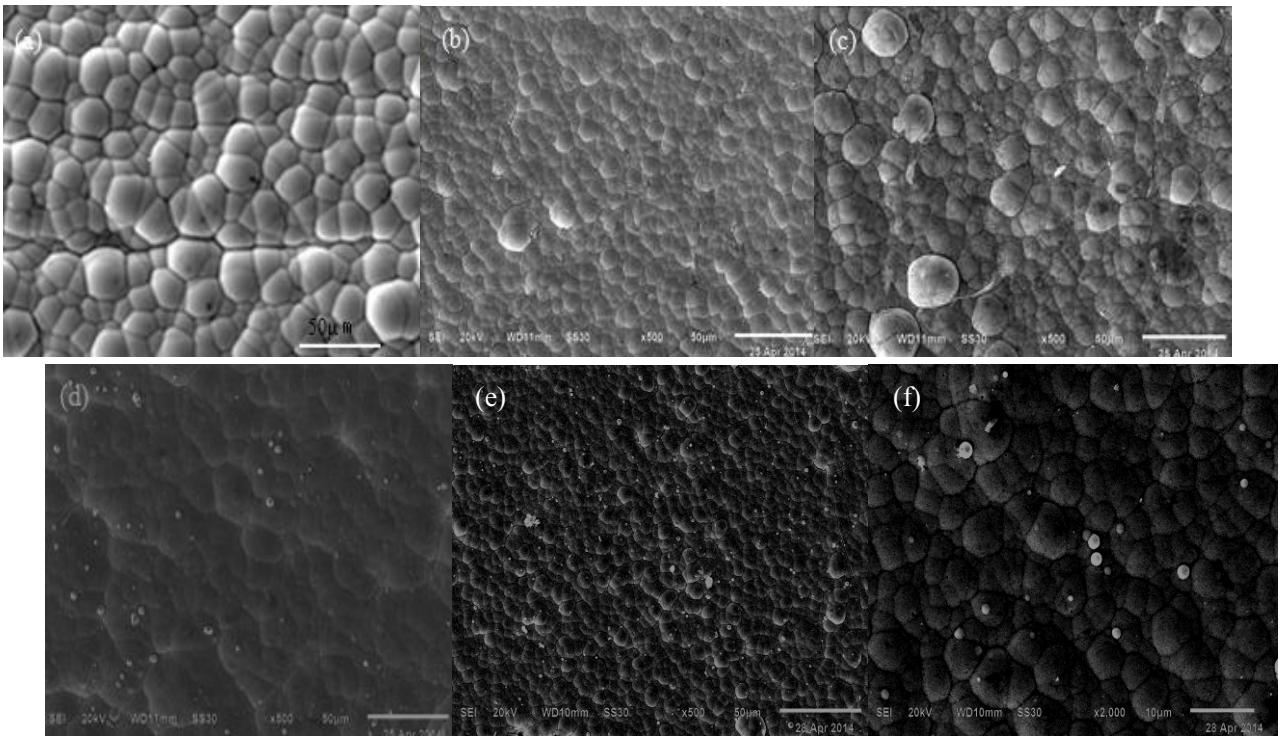

Figure 2 the surface morphology of magnesium matrix composite coatings (2h plating time, a: no SiC or TiO_2 ; b: SiC 2g/L; c: SiC 5g/L; d: SiC 10g/L; e: TiO_2 2g/L; f: magnification of e)

Many studies have been reported, the wear resistance and hardness of the coatings are improved when adding SiC or TiO_2 particles undoubtedly. Compare map b with map c (in Fig. 1), the coating has the advantages of finer grain, more uniform and no obvious defects.

With increasing concentration of SiC particles, fluoride cannot effectively prevent agglomeration of particles, the large size package was emergence on the coating surface when adding 10g/L SiC , it may be because by SiC particles aggregates or the nickel-phosphorus plating's formation of the SiC as an active center in the package. When 2000X morphology of picture d (in Fig.1), many holes and sizes packages on the coating surface can be found (Fig.2). Characterized by electron probe, Ni, P, Si and other elements were found in the package. The reason maybe the SiC particles deposited directly in the coating, and covered with a thin layer of Ni-P plating. when electron probe characterization this Ni-P plating layer, the plating was broken , then the Ni, P, Si and other elements were obtained. The agglomeration of SiC particles caused the coating more loose and holes increased, which is consistent with the results of Xiu Chen, etc.[6] studies.

Electron probe detection

The surface morphology of magnesium matrix composite coatings (SiC=2g/L) were detected by electron micro-probe (EPMA). The results show that: nickel is the highest content of plating, 84.62%, phosphorus is 9.26% (lower than the general electroless Ni-P coating[7,8]), Si and C are 2.6%, a small amount of Oxygen element is detected too. Pure Ni-P coating with good corrosion resistance, because of the rich P phosphate coating film formed on the surface which has a strong corrosion resistance, could protect the matrix effectively. But the SiC particles' addition in the coating, caused phosphorus content decrease, which unfavorable the corrosion resistance of the composite coatings.

Corrosion behavior of Coating

E-t curve

The measurement of potential-time (E-t) curve was started after the electrode immersed in 3.5%

NaCl solution for 10min, showed in Fig. 3. It was found that, the corrosion rate of coatings is faster at the beginning 10 min, and about 15min later, the corrosion rate is gradually stabilizing. As can be seen from the figure, the corrosion potential of the substrate is about -1.5V, corrosion potential of pure Ni-P coating is about -0.5V, corrosion potential Ni-P-TiO_2 composite coating is about -0.8V, lower than corrosion potential Ni-P-SiC composite coating (-0.75V). Relative to the substrate, both the coatings corrosion potential are improved. Coatings on the substrate played a protective role in some degree.

The polarization curves

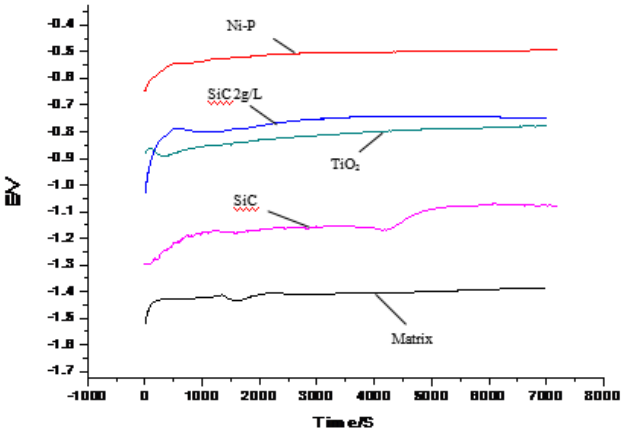

Fig.3 E-t curves of coatings and magnesium matrix composites

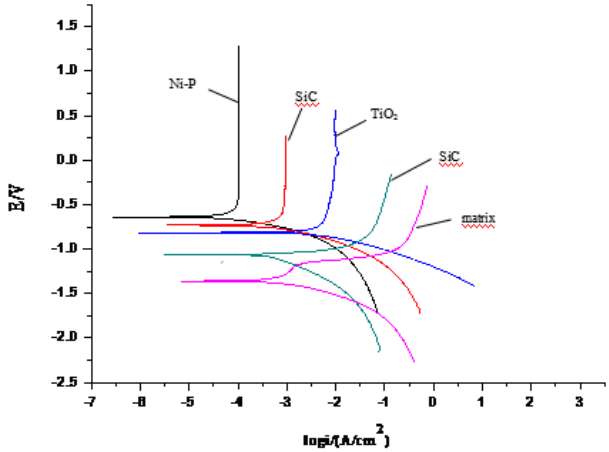

Fig.4 polarization curves of coatings and magnesium matrix composites(in 3.5%NaCl)

The magnesium matrix composite substrate and coatings polarization curves are showed in Fig. 4. It can be seen from the figure, the coatings passivation were occurred in the anode region at different levels. Pure Ni-P coating Passivation is particularly evident, SiC and TiO_2 particles decreased the corrosion resistance of the coating.

SiC or TiO_2 affects the corrosion resistance of the coating, the reasons are the following: (1) SiC or TiO_2 particles uniformly distributed in the coating, played the role of dispersion strengthening, thereby increasing the hardness of the composite coatings[9,10]. However, SiC or TiO_2 caused coating loose and increased porosity when SiC or TiO_2 was added to the coating, the corrosive media easy to penetrate the coating from porosity, the corrosion resistance is decreased. (2) The potential difference exists between the Ni-P, Ni-SiC or TiO_2, and P-SiC or TiO_2, numerous tiny galvanic were formed in the corrosion solution, which accelerated the corrosion and reduced the corrosion resistance of the coating. (3)The content of phosphorus determines the quality of the corrosion resistance of the coating to a certain extent. A stable phosphorus passivation film can be formed in the corrosion solution, which play a good protective effect. The higher phosphorus content, the better corrosion resistance of the coating. When the SiC or TiO_2 particles were added to the coating, the phosphorus content was decreased, so the composite coatings corrosion resistance decreased. This is consistent with the conclusions of Zhang Shusheng, etc. [11] and Lin CJ et al [12] in the study of Ni-P-SiC composite coating's conclusions.

TiO_2 affects the corrosion resistance of the coating significantly higher than the SiC, mainly due to the oxygen-containing. Oxygen ions(O^{2-}) migrate to the surface of the matrix, will react with magnesium,then the electron of the magnesium will migrate to the coating surface through TiO_2 , reacts with the oxygen in the air. The reaction accelerate the corrosion of the magnesium matrix.

AC impedance spectroscopy

AC impedance spectroscopy of coating and substrate in corrosive medium (3.5%NaCl) are

shown in Fig. 5. There is an incomplete high-frequency capacitive loop in Ni-P coating and Ni-P-SiC(2g/L) composite coating, and no inductive loop in the fourth quadrant, which indicate that the film resistance is larger. Ni-P coating and Ni-P-SiC(2g/L) composite coating have good corrosion resistance. In contrast, Ni-P-TiO_2(2g/L) and Ni-P-SiC(10g/L) composite coatings exhibit two capacitive loops. The emergence of the low-frequency capacitive loop indicated that the passivation film was regenerated on the substrate after the film was erosion. All these indicate that the coating corrosion resistance is poor.

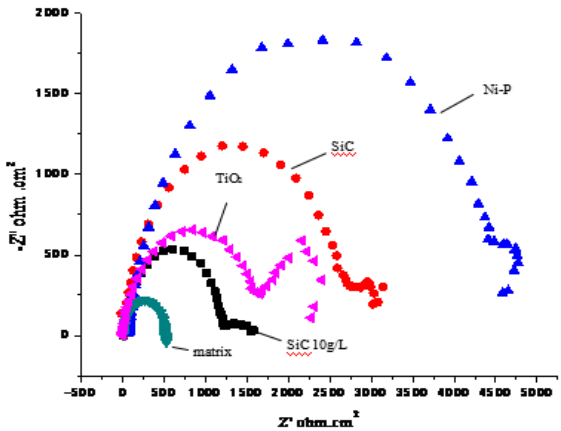

Fig. 5 AC impedance spectroscopy of coatings and magnesium matrix composites(in 3.5%NaCl)

Binding force test

File experiments: File and the coating surface is 45º, exposing the substrate and coating interface, the coating isn't peeling or shedding. Thermal shock experiments: The sample is placed in an incubator for 30min at 200 ℃, then put into the cold water, repeated tests for 10 times, the coating without peeling, flaking and other phenomena, indicating the coating and substrate is good.

Conclusions

(1) Basic nickel carbonate salt formulations suitable for magnesium matrix composite to electroless nickel-based composite coating. Nano-SiC or nano-TiO_2 concentration of 2g/L is appropriate.

(2) When SiC concentration is 2g/L, nickel content was 84.62%, phosphorus was 9.26% and SiC was 5.2% in the composite coating.

(3) The porosity was increased with increasing concentration of SiC or TiO_2 particles. Corrosion resistance of coatings decreased, but compared with the magnesium matrix composite substrate the corrosion resistance was improved.

(4) The corrosion potential of the substrate is about -1.5V, corrosion potential of pure Ni-P coating is about -0.5V, corrosion potential Ni-P-TiO_2 composite coating is about -0.8V, lower than corrosion potential Ni-P-SiC composite coating (-0.75V).

Acknowledgments

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