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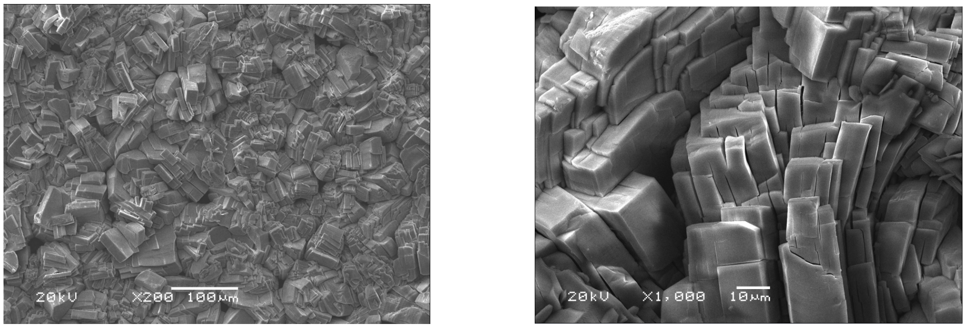
Graphical Abstract



（a） （b）

Zinc-manganese phosphate conversion coatings have been formed on magnesium-lithium alloy and can enhance corrosion resistance of the alloy.

Characteristics and corrosion studies of zinc-manganese phosphate coatings on magnesium-lithium alloy

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Abstract

Zinc-manganese based conversion coating on magnesium-lithium alloy has been prepared from a phosphate solution at different pH value. The surface morphology and composition of the coating were characterized by scanning electron microscopy (SEM), energy dispersion spectroscopy (EDS), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), and corrosion resistance of the coating was studied by potentiodynamic polarization curves, electrochemical impedance spectra (EIS) and corrosion weight loss measurement. The experimental results indicated that the coating with large crystals were homogeneous and ordered. The coating consists of Zn, $Zn_3(PO_4)_2$ and $MnHPO_4$. The corrosion resistance of the magnesium-lithium alloy has been improved by the treating of phosphate conversion.

Keywords: Magnesium-lithium alloy; zinc-manganese; phosphate conversion coating; corrosion resistance

1. Introduction

Magnesium–lithium alloys are the lightest structural metallic alloys and currently available [1, 2]. And they possess high specific strength, excellent formability, impact properties, damping capacity and resistivity of energetic particles penetration. The addition of lithium to magnesium causes a considerable weight saving and makes them lighter than conventional magnesium alloys. Undoubtedly, they are the most promising materials in light-weight engineering applications, such as aerospace field,

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weapon, automotive and electronics industries, etc.[3]. Besides, magnesium-lithium alloys have many advantages: high electrical and thermal conductivity, good ratio of strength to weight, high ability to dampen shock waves, easy forming at room temperature and so on [4]. However, Mg-Li alloys have some disadvantages, particularly their poor corrosion resistance and wear. The corrosion of Mg–Li alloys is more serious than other Mg alloys because Li possesses high chemical activity, which greatly hinders their use in practice. Therefore, it is urgently necessary to find a suitable protection method to improve the corrosion resistance of magnesium–lithium alloys.

There are a number of available methods to protect magnesium alloys against corrosion, including conversion coating[5], anodizing[6], vapor-phase processes[7], electroless plating[8], organic treatment, diamond-like carbon (DLC) coating[9] and laser surface modification technique[10]. Among them, the conversion coating treatment is widely used because of comparatively cheap and easily operating. It is well known that conversion coating based on chromate ions is the traditional method. However, chromate is unfriendly to the environment. The chromate solution is being progressively restricted due to the high toxicity of the hexavalent chromium compounds [11]. Recently, lots of chromate free conversion coatings have been developing, such as molybdate conversion coatings, rare earth conversion coatings and stannate conversion coatings, etc[12-14]. A certain mount of phosphate conversion coatings on magnesium alloys have been obtained. Mosiałek M. [15] has prepared conversion coatings on the AZ81 magnesium alloy by using the different composition phosphate-permanganate baths. Zeng R. [16] has prepared zinc phosphate coating and zinc-calcium phosphate coating on the surface of AZ31 Mg alloy in phosphate baths. The Zn-Mn phosphate coatings are used maturely on the steel surface, which shows the better corrosion resistance. Nikdehghan, H. et al [17] has investigated the corrosion resistance of Zn-Mn phosphate coatings on the steel surface.

However, little information about the zinc-manganese phosphate conversion coating treatment on magnesium-lithium alloys has been reported.

The aim of this study is to develop the zinc-manganese phosphate conversion coating on magnesium-lithium alloy. The process only employs $Zn(H_2PO_4)_2$ and $Mn(NO_3)_2$ as the essential precursors, which makes the coating process easier and greener. Effect of pH value on the corrosion resistance of the zinc-manganese phosphate conversion coating is investigated. The morphology and composition of this coating are also examined.

2. Experiments

2.1 Preparation of conversion coating

Mg-8.5Li alloy is employed for this study. Its chemical compositions are as follows (in wt.%): Al 3.2, Li 8.5, Y 1.2, Ce 1.2 and Mg balance. All samples are from the same kind of casting, and prepared from Mg-Li alloys with the size of 15mm×15mm×7mm.

Prior to formation of conversion coating, specimens were successively polished with 800#, 1500#, 2000# and 3000# by the abrasive paper to obtain a smooth surface, and pretreated with alkaline degreasing and acid pickling[19], then were treated in phosphate solution and respectively rinsed twice in flow distilled water between each step to remove all the contaminations. The phosphate bath for deposition of conversion coating contained $Zn(H_2PO_4)_2$ 50g/L, NaH_2PO_4 20 g/L, 50%$Mn(NO_3)_2$30 g/L, $C_6H_8O_7$ 5g/L, $C_{18}H_{29}NaO_3S$ 0.2 g/L and pH value was adjusted by H_3PO_4 to 1.8-2.6. The temperature was 45 ^{o}C and deposition time was 15 min, and then dried in hot air.

2.2 Characterization of the coating

The morphologies of conversion coating were examined by JSM-6480A scanning electron microscopy （SEM）and the energy spectrum images were equipped with energy dispersion spectroscopy（EDS）.

The chemical composition of the coating was probed by using Physical Electronics, PHI 5700 EICA X-ray photoelectron spectroscopy (XPS) with Al $K\alpha$ (1486.6 eV) monochromatic source. Data was taken after 120 s of ion etching. All energy values were corrected according to the adventitious C 1s signal, which was set at 284.62 eV. The data were analyzed with XPSPEAK 4.1 software.

The crystal structure of the alloy and zinc-manganese phosphate conversion coating were determined by X-ray diffraction (XRD) with a glancing incident angle of 2°. The detected angle was from 10° to 80° at a speed of 15°/min. The XRD pattern was analyzed with MDI Jade 5.0 software.

The corrosion resistance of zinc-manganese phosphate conversion coating was studied by electrochemical tests and weight loss measurement. Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization were conducted using a commercial Model CHI760B electrochemical workstation in a three-electrode system with sample (1cm×1cm surface area) as working electrode (WE), saturated calomel electrode as reference electrode (RE) and platinum sheet with 1cm×1cm surface area as counter electrode (CE). The corrosive medium was 3.5 wt.% NaCl solution. The potentiodynamic polarization curves were tested at a scan rate of 0.01V/s. The corrosion potential and corrosion current density were calculated by Tafel extrapolation method using the CHI version 6.28 software (by CH Instruments). The EIS measurements were carried out at open circuit potential, and the frequency range was between 0.01Hz and 100,000 Hz. All of the measurements were carried out at room temperature.

The weight loss experiments were carried out using Mg-8.5Li alloy with phosphate conversion coatings. The samples were firstly dried and weighted (m_1), and suspended in 100 mL solution of 3.5wt. % NaCl for 4h at 25 ^{o}C. Secondly, each sample was washed with distilled water, acetone in an ultrasonic bath, then dried and weighted again (m_2). Weight loss measurements were made in triplicate and the loss of weight was calculated by taking an average of these values.

3. Results and discussion

3.1 Surface morphology and chemical composition of the conversion coatings

After phosphate conversion, a gray smooth coating formed on the Mg-Li alloy surface. Fig.1. shows the surface morphology of Mg-Li alloy after treatment which covers with zinc-manganese conversion solution at the conditions of 45 ℃ and 2.0 of pH value. The coating nearly covers all over the surface of the alloy. The conversion coating consists of crystal clusters with some cracks. It can be observed that the crystal clusters embrace together compactly in the joints. The formation of cracks is possibly due to the release of hydrogen via the chemical reaction during the formation of conversion. It is obvious that the compact crystal clusters can afford better protection than the rare earth conversion coating and molybdate/permanganate conversion coating with dry-mud shape.

The cross-sections of coating at different pH have been analyzed as shown in Fig.2. Fig.2 shows that the substrate is corroded and part of the conversion coating is not complete. Because the conversion coatings present crystal clusters and the chemical property of Mg-Li alloy is activity. The coatings are not complete and Mg-Li alloys are damaged by corrosion ion when the samples are polished. The pH has an influence on the growth. The thickness of coating at 2.0 of pH is the thickest, which indicates the coating at 2.0 of pH may be having a certain protection effect on the substrate.

XPS spectroscopy is a material characterization technique which widely is used to investigate the chemical composition of materials. The XPS results of the Zn-Mn phosphate conversion coatings are displayed in Fig.3.

Fig.3a shows the survey spectra of the Zn-Mn phosphate conversion coatings obtained by XPS and Table 1 shows the detailed XPS results of surface atomic compositions of the conversion coatings. The coating predominantly contains Mg, O, P, Mn and Zn elements. The XPS high-resolution scanning spectra of Mg 1s, P 2p, Mn 2p, Zn 2p and O 1s is depicted in Fig. 3b, Fig. 3c, Fig. 3d, Fig. 3e and Fig. 3f, respectively.

The XPS specific spectra of Mg 1s displayed in Fig. 3b indicates that the peaks at 1303.90 eV and 1302.7 eV correspond to MgO and $Mg(OH)_2$. Fig.3c gives the XPS data of Mn2p spectra peaks at 643.5 eV and 642.5 eV. The result proves that the conversion coating is the compounds of $Mn_3(PO_4)_2$ and $MnHPO_4$. Fig.3d presents the high resolution XPS spectrum of O 1s, which is divided into peaks at 532.5 eV, 531.2 eV, 531.3 eV and 531.7 eV. The peaks at 531.2 eV and 532.5 eV are attributed to PO_4^{3-} and HPO_4^{2-}. The peaks at 531.7 eV and 531.3 eV correspond to O 1s in MgO and $Mg(OH)_2$. Fig.3e shows the high resolution spectrum of P 2p, which can be divided into three peaks: 133.8 eV, 132.9 eV and132.1 eV. The peak at 133.8 eV corresponds to $MnHPO_4$, and the peaks at 132.9 eV and132.1 are attributed to the PO_4^{3-} of $Zn_3(PO_4)_2$ and $Mn_3(PO_4)_2$, respectively. Fig.3f gives the XPS data of Zn 2p spectra peaks at 1021.2 eV and 1021.9 eV which can be attributed to hopeite and Zn. It can be found that zinc takes the form of Zn elementary and $Zn_3(PO_4)_2$. The XPS results indicated that the Zn-Mn phosphate conversion coatings consisted of MgO, $Mg(OH)_2$, $Zn_3(PO_4)_2$, Zn, $MnHPO_4$ and $Mn_3(PO_4)$.

The structure of conversion film is characterized by XRD as shown in Fig.4. The diffraction peaks indicate the existence of Zn, $Zn_3(PO_4)_2$ and $MnHPO_4$. According to the intensity and quantity of the diffraction peaks, it can be speculated that the conversion film contains Zn, $Zn_3(PO_4)_2$, and $MnHPO_4$. The XRD results show great accordance with the XPS analysis.

The possible reactions mechanism for the deposition of Zn-Mn phosphate conversion coatings are analyzed as follows.

The surface of Mg-Li alloy in the acidic phosphate solution was dissolved to produce Mg^{2+} and Li^{+}, accompanying with the hydrogen evolution reaction, resulting to the concentration of OH^{-} increase greatly at the interface of Mg-Li alloy substrate and phosphate solution.

$$Mg - 2e^{-} \rightarrow Mg^{2+} \qquad (1)$$

$$Li - e^{-} \rightarrow Li^{+} \qquad (2)$$

$$2H_2O + 2e^{-} \rightarrow 2OH^{-} + H_2 \qquad (3)$$

Then $H_2PO_4^{-}$ reacts with OH^{-} to form HPO_4^{2-} and PO_4^{3-}. In the acidic phosphate solution, most of HPO_4^{2-} preferentially bonded with Mn^{+} to form insoluble $MnHPO_4$, and most of PO_4^{3-} preferentially bonded with Zn^{2+} to form insoluble $Zn_3(PO_4)_2$ and $Mn_3(PO_4)_2$.

$$H_3PO_4+OH^{-}\rightarrow H_2PO_4^{-}+H_2O \qquad (4)$$

$$H_2PO_4^{-}+OH^{-}\rightarrow HPO_4^{2-}+H_2O \qquad (5)$$

$$HPO_4^{2-}+OH^{-}\rightarrow PO_4^{3-}+H_2O \qquad (6)$$

$$2PO_4^{3-}+3Zn^{2+}\rightarrow Zn_3(PO_4)_2(s) \qquad (7)$$

$$HPO_4^{2-}+Mn^{2+}\rightarrow MnHPO_4(s) \qquad (8)$$

$$2PO_4^{3-}+3Mn^{2+}\rightarrow Mn_3(PO_4)_2(s) \qquad (9)$$

$$3Mg^{2+}+2PO_4^{3-}\rightarrow Mg_3(PO_4)_2 \qquad (10)$$

A handful of the Zn^{2+} reduces to Zn elemental, which deposits on the conversion film accompanying with the insoluble phosphate. And in the acidic phosphate solution, the Zn^{2+} ions which are from $Zn(H_2PO_4)_2$ reduce to the metallic zinc on the substrate. The reactions are as follows:

$$Mg+Zn^{2+}\rightarrow Zn(s)+Mg^{2+} \qquad (11)$$

$$2Li+Zn^{2+}\rightarrow Zn(s)+2Li^{+} \qquad (12)$$

When the phosphate film nearly covers all over the magnesium-lithium alloy surface, the phosphate reaction will stop.

Energy dispersive spectra of the phosphate coating are presented in Fig.5. Fig.4a shows the surface morphology (×250) of the Zn-Mn phosphate conversion coatings prepared at the 2.6 of pH value under 45 ^{o}C. From microcosmic aspect, the elemental mapping (Fig. 5b) is achieved to determine the elemental distribution of O, Mg, P, Zn, Li and the trace of Mn. It can be seen that O, Mg, P, Zn, Li and Mn distribute homogeneously on the surface. Mg and Li belong to the dominant component substrate. It further indicates that both substrate and electrolyte make a contribution to the formation of coating. It is consistent with the XPS result.

3.2 Corrosion resistance of conversion coating

3.2.1. Electrochemistry characterization

Fig.6 shows the potentiodynamic polarization curves of bare Mg–Li alloy and Mg–Li alloy with Zn-Mn phosphate conversion coating at various pH value in 3.5 wt. % NaCl solution. The results of corrosion potential (E_{corr}) and corrosion current density (I_{corr}) are listed in table 2. It clearly shows that the corrosion resistance of the specimen with Zn-Mn phosphate conversion coating is enhanced when pH value is 2.0. The specimen with conversion coating shows corrosion potential (V_{SCE}) is much more positive than that of the bare alloy (V_{SCE}). The corrosion current density of the conversion coating is 5.004×10^{-6}A/cm^2 at 2.0 of pH value which was one order lower than that of molybdate conversion coating (1.843×10^{-5} A/cm^2)[12]. Thereby the corrosion resistance of Zn-Mn phosphate conversion coatings is better than the molybdate conversion coatings. Zn-Mn phosphate conversion coatings can provide good protection for the Mg-Li alloy (1.294×10^{-4} A/cm^2). These results explain that the coated samples at 2.0 of pH value have better corrosion resistance than the substrate. In the polarization curves the cathode reaction corresponds to the formation of the hydrogen, and the active dissolution reaction of anodic control is the most important feature which relates to the corrosion resistance [15].

The pH has the influence on the growth and thicknesses of Zn-Mn phosphate coatings, which leads the different corrosion current density. With the decreasing pH value, the corrosion current density of conversion coating decreases, when pH value is 2.0, the corrosion current density reached minimum. However at 1.8 of pH the phosphating reaction is violent, too much hydrogen on the Mg-Li alloy surface makes the phosphide cannot deposite on the subtrate easily, the phosphate conversion coating become loose, porous, thin and nonuniform and corrosion current density increased. When pH value becomes higher, the reaction rate becomes lower, the depositing of the phosphide becomes more difficult and the corrosion current density increases.

The electrochemical impedance spectroscopy of bare Mg–8.5Li alloy and the alloy with phosphate conversion coatings are recorded at open circuit potential in 3.5 wt. % NaCl solution. The Nyquist plots are shown in Fig. 7. All the samples contain a single capacitive semicircle according to the plot. And the diameter of the capacitance loop of the phosphate samples coated at the 2.0 of pH solution is larger than that of the samples coated at other pH values, which indicates the better corrosion resistance of phosphate conversion coating. And the diameter of the capacitance loop when the pH value of the Zn-Mn phosphate conversion coating is 2.0 is bigger than that of the molybdate conversion coating [12] and Zn phosphate coating[16]. It indicates that the phosphate conversion coating obtained at the 2.0 of pH value presents the most active behavior, which is agreed with the potentiodynamic polarization results.

3.2.2. Corrosion weight loss measurement

Corrosion weight loss is an average measurement which is determined by change of the quality of samples before and after corrosion. Corrosion rate can be calculated from the equation: $v= (m_1-m_2)/s\cdot t$. Where m is the weight before and after exposure in corrosion media, (m_1-m_2) is the weight loss in grams, s is the total surface area in m^2, t is the time of exposure in h, and v is the corrosion rates in $g/(m^2 \bullet h)$.

The weight loss method is the most fundamental measurement to quantify corrosion attack in laboratory experiments. Fig.8 shows the corrosion rate of phosphate conversion coatings at different pH value in 3.5 wt. % NaCl solution at room temperature for 4 h. The samples weight decreased after immersing, which indicates dissolution of the coating. Based on the weight loss data, it is observed that the phosphate conversion coating in the solution at 2.0 of pH has lower corrosion rate and the order is in accord with the EIS result.

4. Conclusions

A conversion coating with uniform and block-like morphology is formed on the Mg–Li alloy in phosphate solution. The phosphate conversion coating mainly consists of Zn, $Zn_3(PO_4)_2$ and $MnHPO_4$. The corrosion resistance of the magnesium-lithium alloy has been improved by the phosphate conversion treatment, and is better than the molybdate conversion coatings. When the pH value is 2.0, the coating obviously reduces the corrosion current density, and the conversion coating presents the best corrosion resistance behavior, comparatively.

Acknowledgements

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References

[1] C. X. Ma, Y. Lu, P. P. Sun, et al. Surface and Coatings Technology. 206 (2011) 287-294.

[2] M.C. Lin, C.Y. Tsai, J.Y. Uan. Corrosion Science. 51 (2009) 2463-2472.

[3] Y. B. Ma, N. Li, D. Y. Li, et al. Materials Letters. 90 (2013) 11-13.

[4] D. X. Cao, L. Wu, Y. Sun, et al. Journal of Power Sources. 177 (2008) 624-630.

[5] J.F. Li, Z.Q. Zheng, S.C. Li , et al. Materials Science and Engineering A. 433 (2006) 233-240.

[6] A. Yabuki, M. Sakai. Corrosion Science. 51 (2009) 793-798.

[7] T. C. Chang, J. Y. Wang, C. L. Chu, et al. Materials Letters. 60(2006)3272-3276.

[8] L. H. Yang, J. Q. Li, Y. Z. Zheng, et al. Journal of Alloys and Compounds. 467 (2009) 562-566.

[9] N. Yamauchi, N. Ueda, A. Okamoto, et al. Surface and Coatings Technology. 201 (2007)

4913-4918.

[10] T. A. Samman. Acta Materialia. 57(2009) 2229-2242.

[11] A. K. Sharma, R. Uma Rani, S. M. Mayanna, Thermochim. Acta. 376(2001)67-75.

[12] G. X. Wang, M. L. Zhang, R. Z. Wu, et al. Applied Surface Science. 258 (2012) 2648-2654.

[13] L.H. Yang, M.L. Zhang, J.Q. Li, et al. Journal of Alloys and Compounds 471 (2009) 197-200.

[14] X. W. Yang, G. X. Wang, G. J. Dong, et al. Journal of Alloys and Compounds. 487 (2009) 64-68.

[15] M. Mosiałek, G. Mordarski, P. Nowak, et al. Surface and Coatings Technology. 206 (2011) 51-62.

[16] R. C. Zeng, Z. D. Lan, L. H. Kong, et al. Surface and Coatings Technology. 205 (2011) 3347-3355.

[17] H. Nikdehghan, A. Amadeh, A. Honarbakhsh-Raouf, Surf. Eng. 24 (2008) 287.

Figure Captions

Fig.1. Surface morphology of zinc-manganese phosphate conversion coating on Mg-Li alloy (a) 200×; (b) 1000×

Fig.2. The cross-section view of the coating at (a) 1.8 of pH; (b) 2.0 of pH; (c) 2.2 of pH; (d) 2.4 of pH; (e) 2.6 of pH.

Fig.3. XPS analyses of the Zn-Mn phosphate conversion coating

Fig.4. XRD pattern of phosphate conversion film.

Fig.5. Surface morphology and elemental mapping of the Zn-Mn phosphate coating on the magnesium-lithium alloy(a) conversion coating treatment under the conditions of 45℃ and the pH value 2.6; (b) elemental mapping

Fig.6. Potentiodynamic polarization curves with various pH value of Mg–Li alloy in 3.5 wt.% NaCl solution.

Fig.7. EIS plots of Mg–Li alloy prepared with various pH value in 3.5% NaCl solution.

Fig.8. The change of the corrosion rate to pH value of substrate and phosphate conversion coatings in 3.5% NaCl solution

Table 1. The XPS results of surface element compositions of Zn-Mn phosphate conversion coating

Element	Al	P	O	Mn	Zn	Mg
Atomic %	2.98	15.35	64.69	0.46	3.38	13.16

Table 2. Parameters of polarization curves

Samples	I_{corr} (A/cm^2)	E_{corr}(V_{SCE})
Bare Mg–Li alloy	1.294×10^{-4}	-1.571
pH=1.8	8.837×10^{-5}	-1.366
pH=2.0	5.004×10^{-6}	-0.370
pH=2.2	6.401×10^{-5}	-1.517
pH=2.4	8.180×10^{-5}	-1.520
pH=2.6	1.058×10^{-4}	-1.071

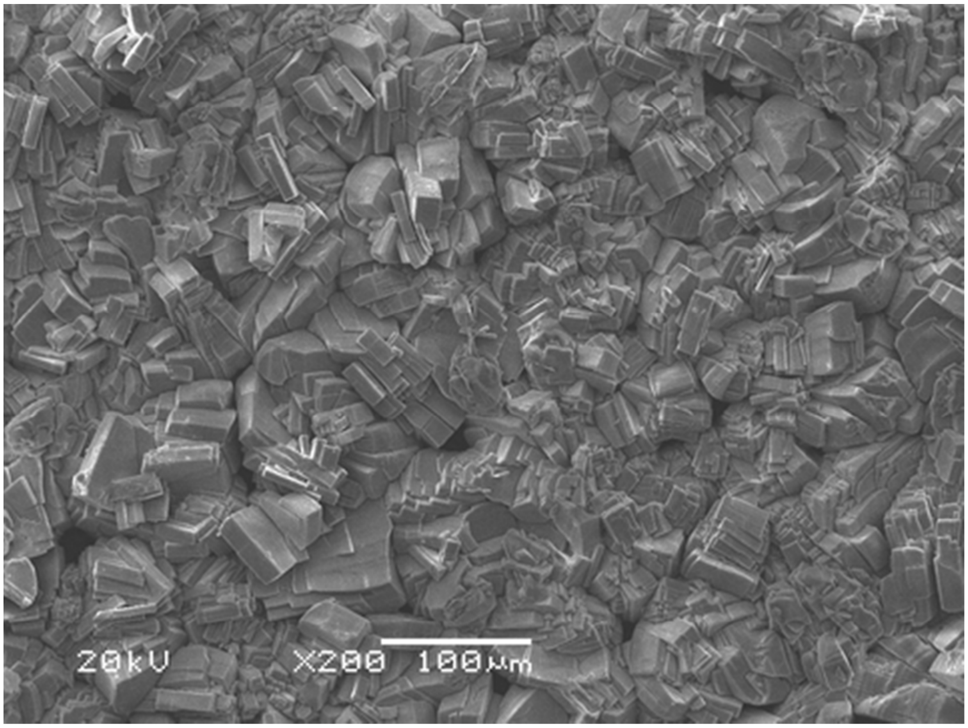
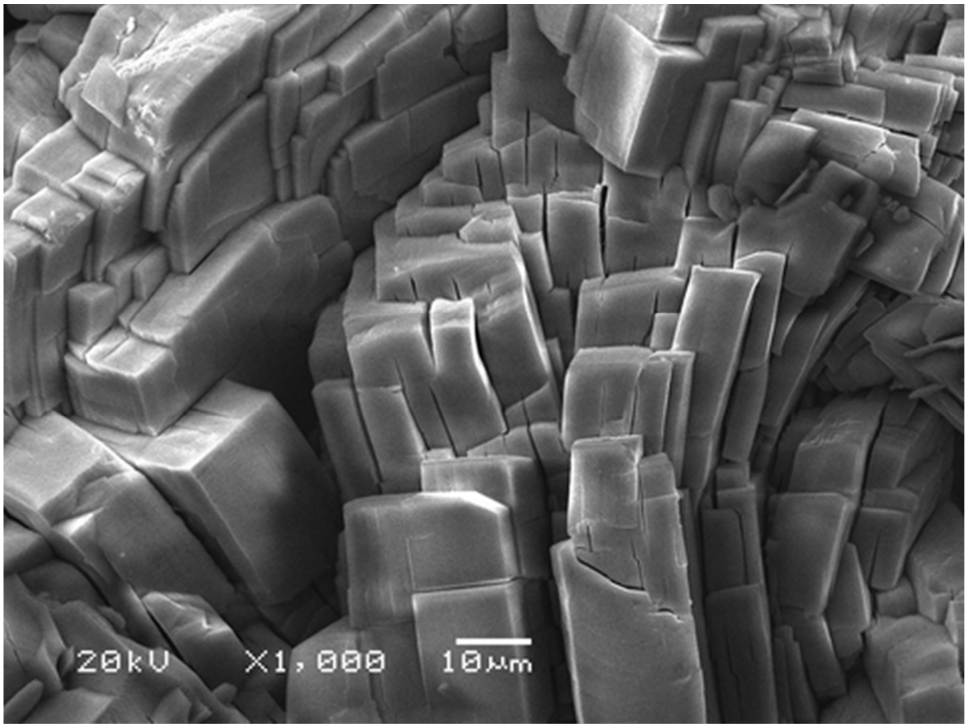


Fig.1. Surface morphology of zinc-manganese phosphate conversion coating on Mg-Li alloy (a) 200×; (b) 1000×
40x30mm (300 x 300 DPI)



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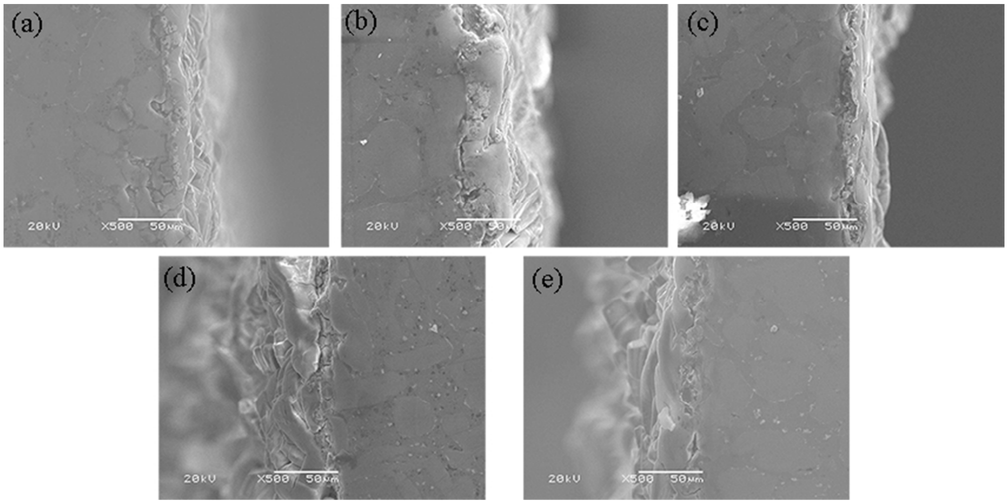


Fig.2. The cross-section view of the coating at (a) 1.8 of pH; (b) 2.0 of pH; (c) 2.2 of pH; (d) 2.4 of pH; (e) 2.6 of pH.
299x149mm (72 x 72 DPI)

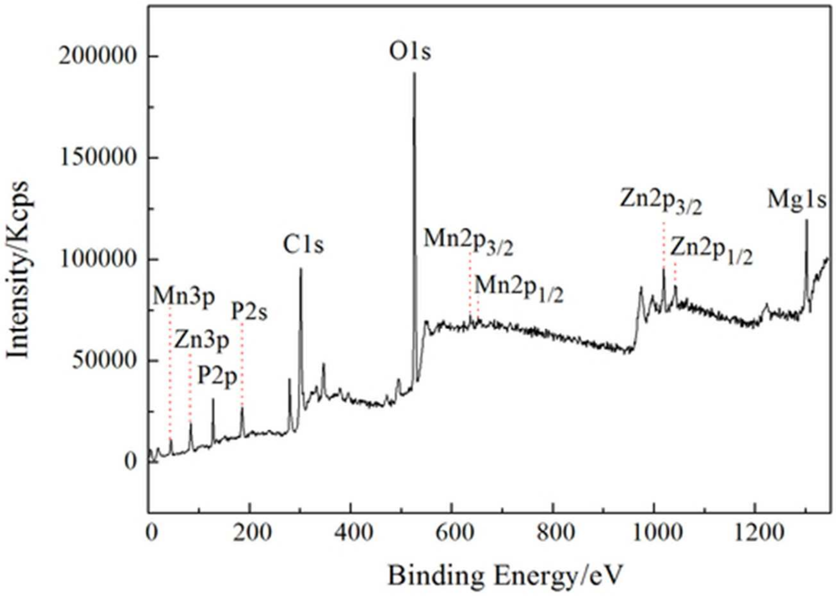
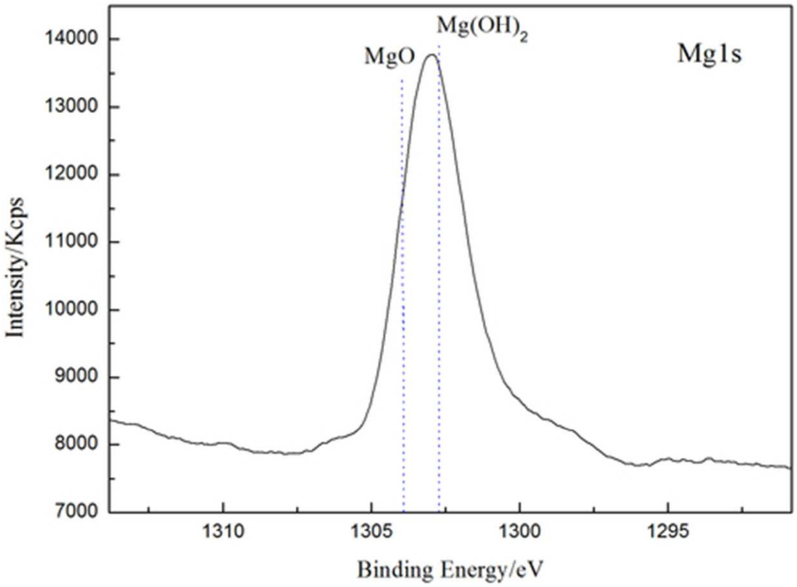


Fig.3. XPS analyses of the Zn-Mn phosphate conversion coating
52x37mm (300 x 300 DPI)



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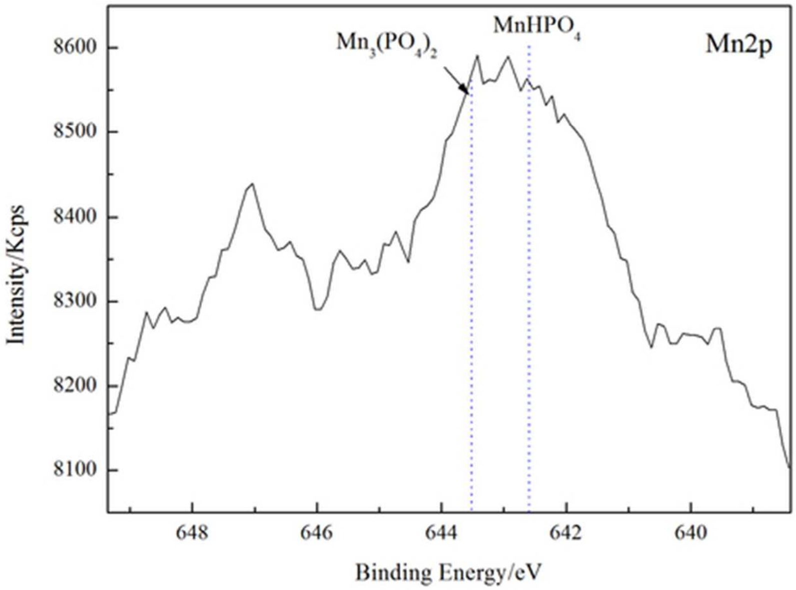
52x37mm (300 x 300 DPI)



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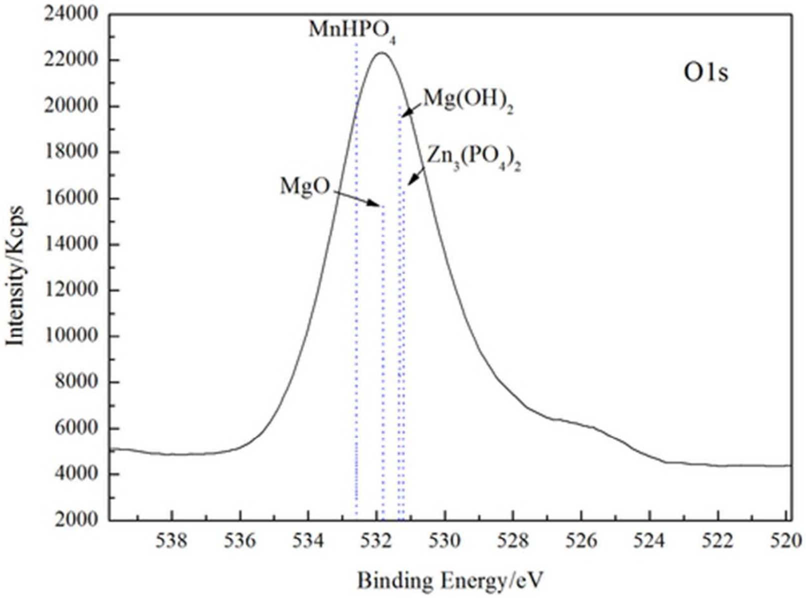

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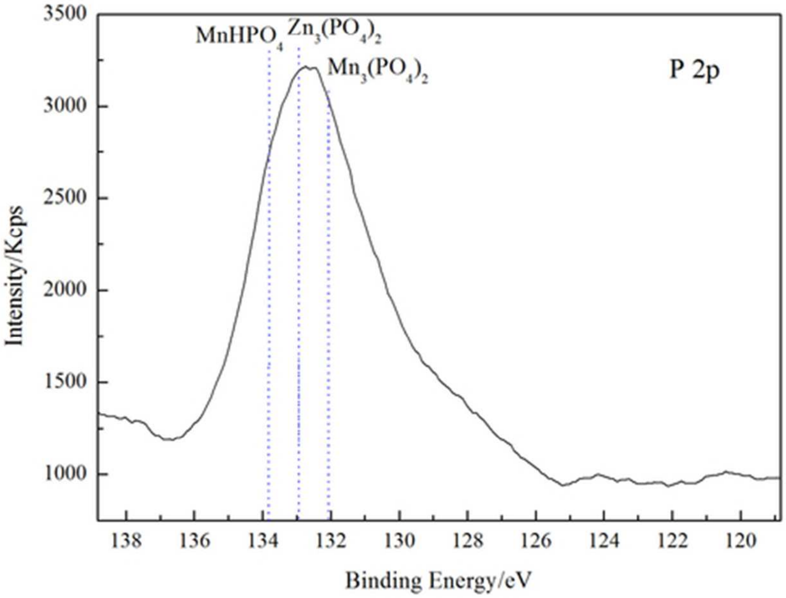

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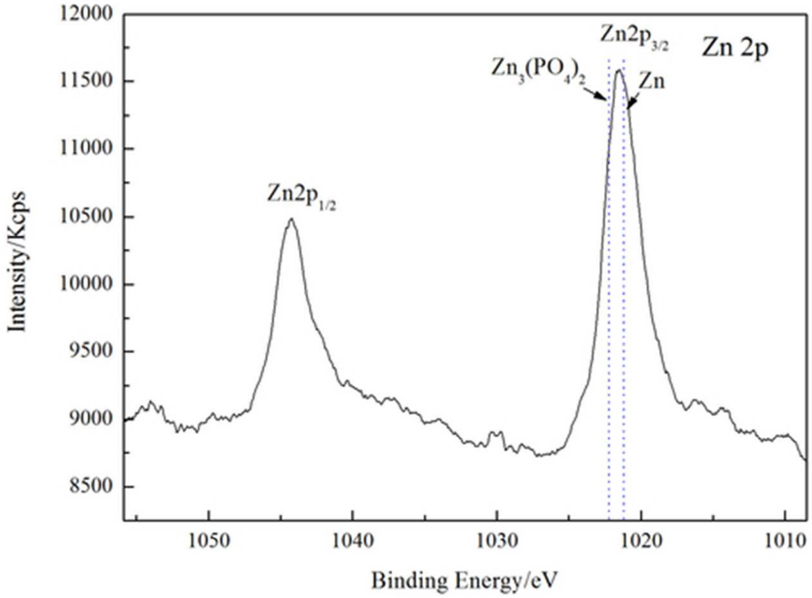

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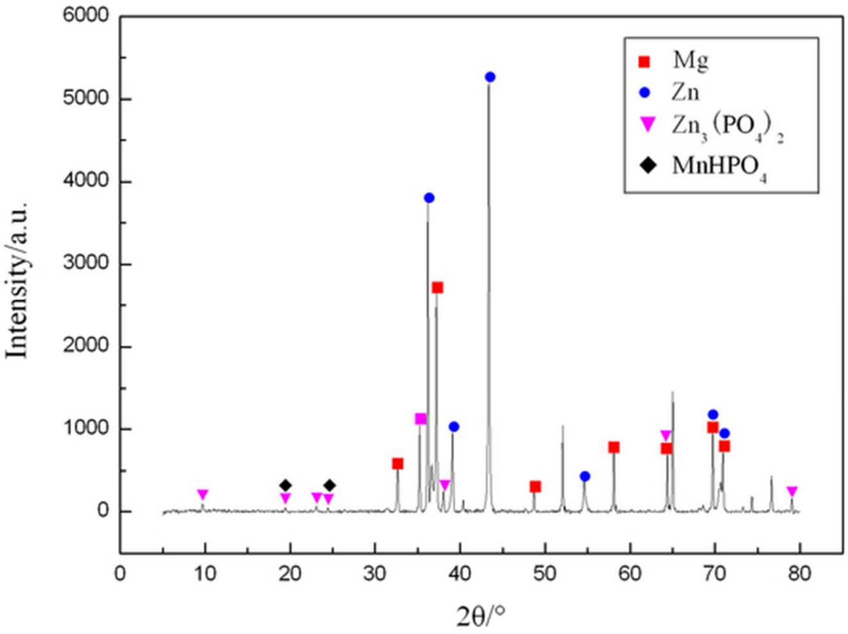

Fig.4. XRD pattern of phosphate conversion film.
54x42mm (300 x 300 DPI)

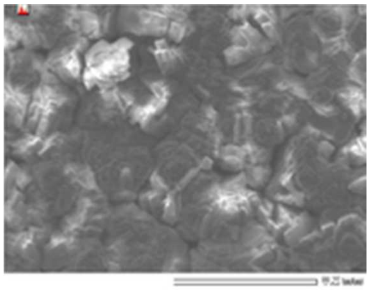

Fig.5. Surface morphology and elemental mapping of the Zn-Mn phosphate coating on the magnesium-lithium alloy(a) conversion coating treatment under the conditions of 45℃ and the pH value 2.6; (b) elemental mapping
15x12mm (300 x 300 DPI)

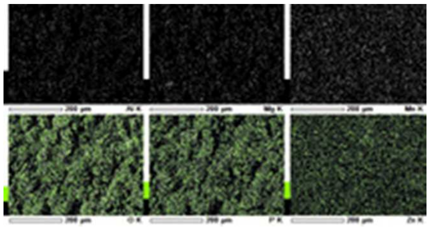

Fig.5. Surface morphology and elemental mapping of the Zn-Mn phosphate coating on the magnesium-lithium alloy(a) conversion coating treatment under the conditions of 45℃ and the pH value 2.6; (b) elemental mapping
17x9mm (300 x 300 DPI)

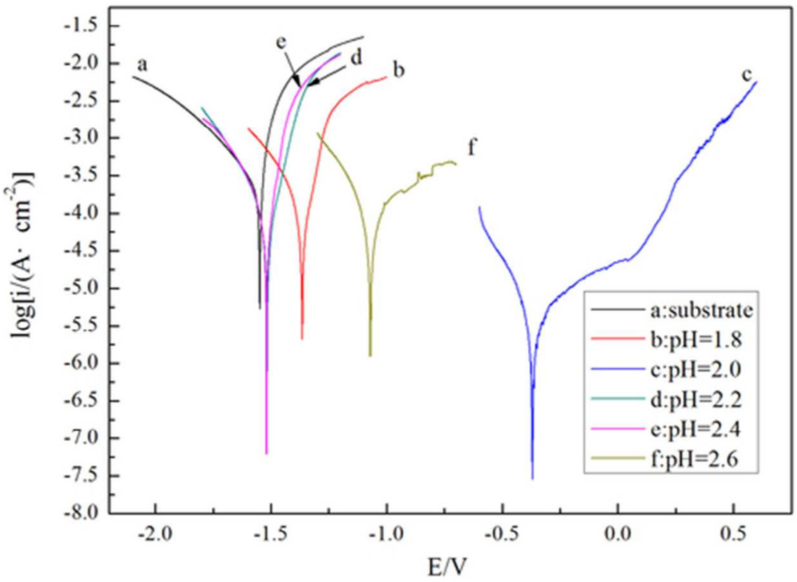

Fig.6. Potentiodynamic polarization curves with various pH value of Mg–Li alloy in 3.5 wt.% NaCl solution.
52x37mm (300 x 300 DPI)

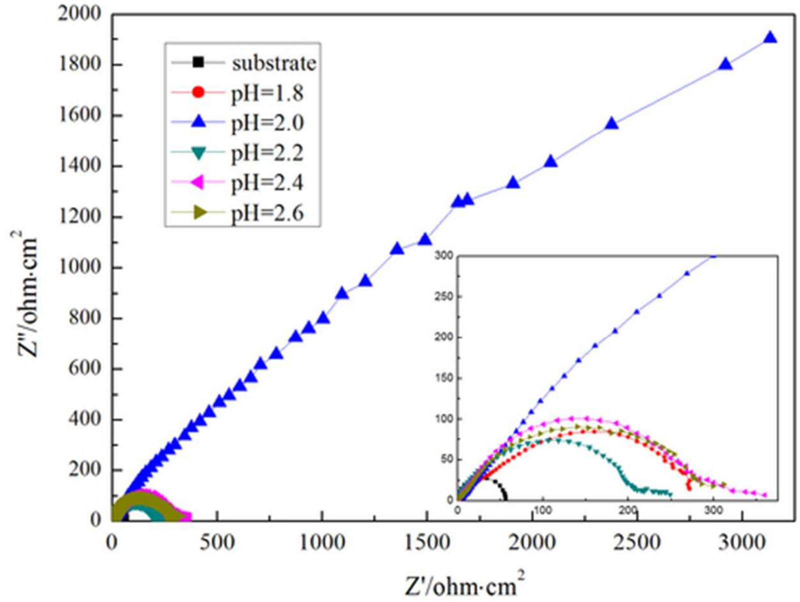

Fig.7. EIS plots of Mg–Li alloy prepared with various pH value in 3.5% NaCl solution.
52x37mm (300 x 300 DPI)

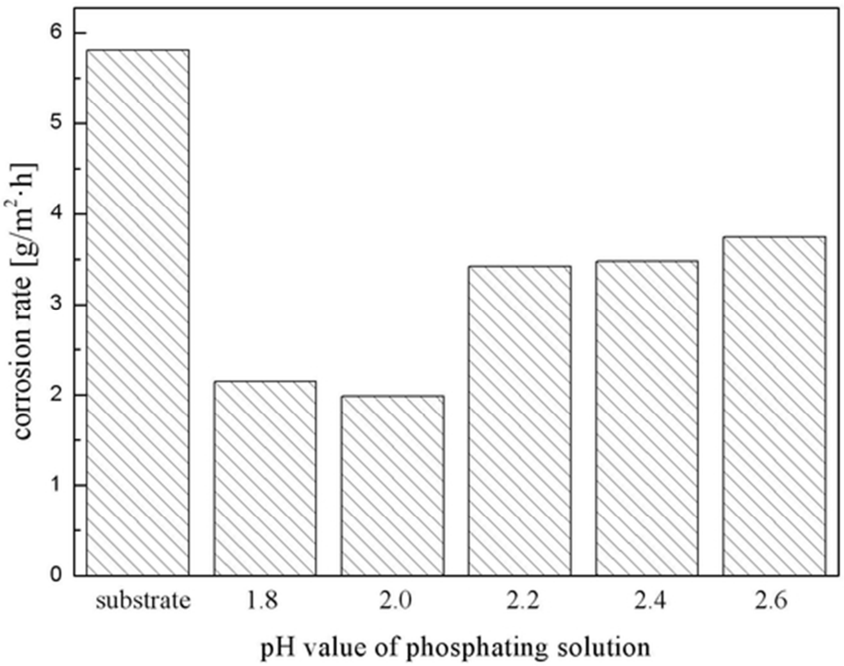

Fig.8. The change of the corrosion rate to pH value of substrate and phosphate conversion coatings in 3.5% NaCl solution
54x45mm (300 x 300 DPI)