

The Structure and Growth Mechanism of Phosphate Conversion Coatings on AZ91D Magnesium Alloy

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ABSTRACT

In this study, AZ91D magnesium alloy is selected as experimental material. Meanwhile, choose zinc phosphate and sodium phosphate conversion solutions to process the experiment. The operating parameters studied included the solution temperature and immersion time. Using SEM, EDS and XRD to observe the surface morphology and analyze the chemical composition of coatings. At the same time, not only measure the thickness and weight of coatings, but examine the adhesives strength and corrosion resistance of conversion coatings by adhesion test and polarization test. From experimental results shown that the zinc phosphate coating contains two layers which including the upper crystalline layer and the lower cracking layer. However, for the sodium phosphate conversion coating, the coating is belong a non-crystalline layer which appear full of cracks and bulk area. The thickness、bulk area and cracks become larger and wider with increasing immersion time. In the aspect of shear strength of coatings, the test of zinc phosphate coating only can obtain the strength between layers, and the value of strength is not quite good. The components of zinc phosphate coating is formed by $Zn_3(PO_4)_2 \cdot 4H_2O$ and $AlPO_4$, which analyzed by EDS and XRD. The $Zn_3(PO_4)_2$ is the major form of compound at the upper crystalline layer. And the components of sodium phosphate coatings is form by $AlPO_4$ and Mg. The test of polarization did show both the zinc phosphate and sodium phosphate coatings can improve the corrosion resistance of the AZ91D magnesium alloy. Comparing the relationship between thickness of coatings and their corrosion current density, we can figure out the capability of resistance from upper crystalline layer is much weaker than the lower cracking layer. We also believed that the main factors determined the corrosion resistance are the thickness of coating, the width of cracks, and the quantity of cracks. Therefore, how to equalize these three factors to obtain the best corrosion resistance are the major concerns. The best operating parameters for zinc phosphate coating is at 45 °C solution temperature and 25 minutes immersion time. If immersion time further increased which will result in the corrosion resistance decreased, the main reason is due to the wideness of cracks in the lower cracking layer increased. While, in sodium phosphate conversion coatings, the thicker the thickness of coating, the performance of corrosion resistance is better, and the best corrosion resistance parameters is under 70 °C and 30 minutes immersion time. Although the performance of corrosion resistance in phosphate conversion coatings is not good as the chromate and vanadate coatings. But these results still can offer a good reference for future study. Hopefully, the researchers can toward the goal of non-chromate coating developing for better anti-corrosive result together.

Keywords : AZ91D Magnesium Alloy, Zinc Phosphate Conversion Treatment, Sodium Phosphate Conversion Treatment, Growth Mechanism, Polarization Curve, Corrosion Current Density.

Table of Contents

封面內頁 簽名頁 授權書	iii	中文摘要	iv	英文摘要	vi		
誌謝	viii	目錄	ix	圖目錄	xii	表目錄	xii
.....	xviii	第一章 前言	1	1.1 鎂合金簡介	1	1.2 鎂合金之應用	1
.....	2	1.3 實驗目標	2	第二章 國內外文獻回顧	5	2.1 金屬表面處理	5
.....	5	2.2 鎂合金表面預處理	5	2.3 鎂合金表面處理流程	6	2.4 鎂合金表面處理種類	8
.....	8	2.4.1 表面預處理	8	2.4.2 電鍍處理	8	2.4.3 陽極處理	8
.....	9	2.4.4 化成皮膜處理	10	2.4.5 金屬覆層	10	2.5 表面處理的功用	11
.....	11	2.6 鎂合金化成皮膜處理	12	2.6.1 磷酸鹽化成皮膜	12	2.6.2 鈮酸鹽化成皮膜	12
.....	19	2.6.3 錳酸鹽化成皮膜	20	2.6.4 鉻酸鹽化成皮膜	23	2.6.5 錫酸鹽化成皮膜	24
.....	24	2.6.6 稀土族化成皮膜	28	第三章 實驗方法	35	3.1 實驗材料	35
.....	35	3.2 實驗規劃	36	3.3 實驗步驟	37	3.4 實驗前處理	38
.....	38	3.5 化成皮膜處理	39	3.5.1 磷酸鋅化成液	39	3.5.2 磷酸鈉化成液	39
.....	39	3.6 化成皮膜處理製程	40	3.7 表面粗糙度的量測	41	3.8 膠接試驗	42
.....	42	3.9 皮膜微觀結構觀察與成份分析	44	3.10 皮膜耐腐蝕性能之極化試驗	45	第四章 實驗結果分析與討論	47
.....	47	4.1 化成皮膜表面形態之SEM觀察	47	4.1.1 磷酸鋅化成皮膜表面形態觀察	47		

.....47	4.1.2 磷酸鈉化成皮膜表面形態觀察53	4.2 磷酸鋅及磷酸鈉皮膜粗糙度的量測57	4.3 磷酸鋅及磷酸鈉化成皮膜厚度的量測60	4.3.1 磷酸鋅化成皮膜厚度量測60	4.3.2 磷酸鈉化成皮膜厚度量測64	4.4 磷酸鋅及磷酸鈉化成皮膜重量量測68	4.4.1 磷酸鋅化成皮膜重量量測68	4.4.2 磷酸鈉化成皮膜重量量測70	4.5 磷酸鋅皮膜試片膠接剪強度試驗72	4.6 磷酸鋅皮膜成份分析(EDS)74	4.7 磷酸鋅皮膜結構分析(X-ray)78	4.8 磷酸鈉皮膜成份分析(EDS)81	4.9 磷酸鈉皮膜結構分析(X-ray)84	4.10 磷酸鋅與磷酸鈉極化曲線量測87	第五章 結論103	第六章 參考文獻105
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REFERENCES

- [1] 蔡幸甫, “輕金屬產業發展現況及趨勢”, 工業材料雜誌, 第198期, pp.72~80, 2003。
- [2] 廖芳俊, 陳家暘, “鎂合金壓鑄件及擠壓件之熔鋸製程探討”, 金屬工業, 第36卷, 第一期, 2002。
- [3] 王俊傑, “鋁鎂合金於汽機車產業之應用發展趨勢”, 大葉大學演講資料, 1999。
- [4] 呂戊辰, “鎂及其合金的表面處理工業”, 表面工業雜誌雙月刊, 第73期, 1999。
- [5] 賴文啟, “鎂鋁合金錳酸鹽皮膜化成處理之研究”, 逢甲大學材料科學研究所碩士論文, 2003。
- [6] 廖漢智, “化成溫度及外加電位對磷酸鋁皮膜性質之影響研究”, 成功大學材料科學及工程研究所碩士論文, 2005。
- [7] 葉信宏、王正全、周雅靜、陳易穗、李秀文, “鎂合金表面處理製程廢料回收再利用”, 永續產業發展雙月刊, 第13期, pp.57~62, 2004。
- [8] 正文編委會, “表面處理法”, 正文書局有限公司, 2005。
- [9] 陳振航、葉明仁, “表面處理之選用與試驗”, 傳勝出版社, 2004。
- [10] L. Kouisni, M. Azzi, M. Zertoubi, F. Dalard, and S. Maximovitch, “Phosphate coatings on magnesium alloy AM60 part 1: study of the formation and the growth of zinc phosphate films”, Surface and Coatings Technology, pp.58~67, 2004。
- [11] L.Y. Niu, Z.H. Jiang, G.Y. Li, C.D. Gu, and J.S. Lian, “A study and application of zinc phosphate coating on AZ91D magnesium alloy”, Surface and Coatings Technology, pp.3021~3026, 2006。
- [12] X. Sun, D. Susac, R. Li, K.C. Wong, T. Foster, and K.A.R. Mitchell, “Some observations for effects of copper on zinc phosphate conversion coatings on aluminum surfaces”, Surface and Coatings Technology, pp.46~50, 2002。
- [13] 楊光綸、宋鈺、葛明德、劉豫川, “鎂合金鈳酸鹽化成皮膜耐蝕性能研究”, 鎂合金產業通訊, 第32期, pp.21~28, 2006。
- [14] 楊承璋, “AZ91D鎂合金化成皮膜結構強度及成長機制之研究”, 大葉大學車輛工程研究所碩士論文, 2005。
- [15] 陳譽升, “AZ31 鎂合金之鉻酸鹽及錳酸鹽化成處理”, 大葉大學機械工程研究所碩士論文, 2004。
- [16] Hingwei Huo, Ying Li and Fuhui Wang, “Corrosion of AZ91D magnesium alloy with a chemical conversion coating and electroless nickel layer”, Corrosion Science, pp.1467~1477, 2004。
- [17] Manuele Dabala, Katya Brunelli, Enrico Napolitani, and Maurizio Magrini, “Cerium-based chemical conversion coating on AZ63 magnesium alloy”, Surface and Coatings Technology, pp.227~232, 2003。
- [18] William G. Fahrenholtz, Matthew J. O'Keefe, Haifeng Zhou, and J.T Grant, “Characterization of cerium-based conversion coatings for corrosion protection of aluminum alloys”, Surface and Coatings Technology, pp.208~213, 2002。
- [19] Yu Xingwen, Cao Chunan, Yao Zhiming, Zhou Derui, and Yin Zhongda, “Corrosion behavior of rare earth metal (REM) conversion coatings on aluminum alloy LY12”, Materials Science and Engineering, pp.56~63, 2000。
- [20] 方國男, “鎂合金錳酸鹽皮膜化成處理”, 大葉大學機械工程研究所碩士論文, 2003。