

# A Study of Corrosion-Resistant Materials in Molten A356 Alloy

柯宗欣、林招松

E-mail: 9612391@mail.dyu.edu.tw

## ABSTRACT

In some industrial implementations, the mechanical elements have prolonged contacts with molten Al or Al alloys, such as the feed screw and barrel of an injection molding machine, which can process molten Al alloy into solid parts, and the rollers in the hot-dip aluminizing bath. These mechanical elements always fail due to the attack of molten Al. This study intends to investigate the corrosion behaviors of the refractory metals, superalloys and metal nitrides to develop the materials suitable for manufacturing the feed screw and barrel of an injection molding machine. Experimental results indicate that heat-resistant steel and IN718 Ni-base superalloy are seriously corroded in molten A356 alloy; thereby forming relatively thick alloy layers on the base materials. Conversely, the metals, such as Nb, W, Ti and Mo, form peritectic alloys with Al and exhibit better corrosion resistance in molten A356 alloy. Furthermore, continuous alloy layer was not observed on Mo-Re and Nb-Ti-W alloys, while these alloys are locally attacked after dipping in molten A356 alloy for 1 to 6 h. In contrast to refractory metals and superalloys, CrN thin film and CrN/TiN multilayer are less corroded in molten A356 alloy. In contrast, TiAlN film is corroded in the early stage of dipping in molten A356 alloy. After certain incubation period, the coated steel was locally attacked, forming hemispherical pits on both CrN and CrN/TiN coated steels. The incubation time for the pit nucleation on the CrN coated steel was shorter than that for the CrN/TiN coated steel. Once the obvious pits formed, the pitted areas increased with dipping time, regardless of the type of coating. After 21 h of dipping, the coating that remained adhering to the steel substrate showed no reaction with the molten Al. The different incubation time of the distinct coatings can be explained by their different coating microstructures. That is, the CrN/TiN coating displayed a finer columnar structure than the CrN coating. The structural refinement resulted from the multilayer coating structure reduced the density of the coating defects. Consequently, the CrN/TiN coating retarded the pit nucleation more effectively than the CrN coating. Additionally, compared to CrN/TiN coating, the surface of CrN coating had more droplets that are potential sites for pit nucleation. Finally, the higher the surface roughness of the steel substrate, the more the corroded area is.

Keywords : metal nitride ; IN718 Ni-base superalloy ; ion nitriding ; CrN ; TiAlN ; CrN/TiN ; droplets ; molten A356 alloy

## Table of Contents

目錄 封面內頁頁次 簽名頁 國家授權書.....	iii 學校授權書.....	
iv 中文摘要.....	v 英文摘要.....	
vii 誌謝.....	ix 目錄.....	
.....x 圖目錄.....		
.....xiii 表目錄.....	.....xvi 第一章 導論.....	
.....1 1.1 前言.....	.....1 1.2 研究動機.....	
.....3 第二章 文獻探討.....	.....4 2.1 半固態程.....	
.....4 2.2 鋁射出成型機料筒與螺桿的功能與所遭遇問題.....	.....6 2.3 物理氣相蒸鍍法製(PVD).....	.....8 2.3.1 離子被覆之理.....
.....9 2.3.2 電弧離子被覆技術原理 (AIP) .....	.....10 2.4 金屬、合金和氮化物與鋁液反應.....	
.....12 第三章 實驗方法.....	.....14 3.1 材料選用.....	
.....14 3.2 浸蝕實驗的設備與方法.....	.....16 3.3 破損程度與評估.....	
.....20 3.4 底材硬度變化.....	.....22 3.5 微觀試片製備與觀察.....	.....22 3.5.1
.....金相試片的準備.....	.....22 3.5.2 縱截面 (平面向) 金相的觀察.....	.....23 3.5.3 掃瞄式電子顯微鏡試片與.....
.....25 3.5.4 穿透式電子顯微鏡試片製作與觀察.....	.....25 3.6 耐熱鋼底材表面粗糙度.....	
.....30 第四章 實驗結果.....	.....31 4.1 高熔點金屬.....	
.....31 4.1.1 銠板.....	.....31 4.1.2 鑷板.....	.....35
.....4.1.3 鉬板.....	.....38 4.1.4 鈦板.....	.....38 4.1.5 鈷板.....
.....42 4.1.6 電鍍鉻耐熱鋼.....	.....42 4.2 高溫合金.....	
.....44 4.2.1 耐熱鋼.....	.....44 4.2.2 718鎳基超合金.....	
.....44 4.2.3 銠合金.....	.....48 4.2.4 鉬合金.....	.....52 4.3
.....金屬氮化物披覆耐熱鋼經機械研磨耐熱鋼：橫截面金相觀察 .....	.....56 4.3.1 氮化鋁鈦披覆未經離子氮化之耐熱鋼.....	
.....離子氮化之耐熱鋼.....	.....56 4.3.2 氮化鉻披覆未經離子氮化之耐熱鋼.....	.....56 4.3.3 氮化鉻披覆經離子氮化之耐熱鋼.....

.....	58 4.3.4 氮化鉻/氮化鈦多層膜披覆經離子氮化之耐熱鋼	64 4.4 金屬氮化物披覆經機械拋光耐熱鋼耐熱鋼.....
...74 4.4.1 氮化鉻披覆經離子氮化之耐熱鋼	74 4.4.2 氮化鉻/氮化鈦多層膜披覆經離子氮化之耐熱鋼	75 4.5 氮化 鉻和氮化鉻/氮化鈦多層膜微結構
.....	84 4.6 金屬氮化物披覆耐熱鋼之表面破損面積.....	91 4.7 各種金屬之硬度變 化.....
91 第五章 討論 .....	98 5.1 各種金屬底材之抗鋁液腐蝕能力	98 5.2 金屬氮化物披覆耐熱鋼.....
.....	99 5.3 破損評估方法.....	100 第六章 結論 .....
104 第七章 展望 .....	108 參 考文獻.....	109 附錄一 底材被鋁侵蝕的示意圖 .....
114 附錄二 金屬 液滴的形成 .....	115	

## REFERENCES

- 1.J. Mihelich and R. F. Decker: US patent 5,819,839, 1998. 2.J. Mihelich and R. F. Decker: US patent 5,711,366, 1998. 3.D. R. Lide ed., Handbook of Chemistry and Physics, 74th ed., CRC press Inc., 1994, 12-155. 4.Y. Wang, "A Study of PVD Coatings and Die Materials for Extended Die-casting Die-life," Surface and Coating Technology, Vol. 94-95, 1997, pp. 60-63. 5.R. R. Aharonov, S. Chellapilla, B. Janoss, K. Shivpuri and A. Lakare, "An Investigation of the Corrosion of H13 Steel Coated with CrN in Molten Aluminum Alloys: Effect of Steel Surface Preparation and Coating Thickness," paper T99-113, Trans., NADCA, International Die Casting Congress. 6.H. Baker ed., ASM Handbook, Vol. 3, 1992. 7.N. Tunca, G.W.Delamore and R.W.Smith, "Corrosion of Mo, Nb, Cr, and Y in Molten Aluminum," Met. Trans., Vol. 21A, 1990, pp. 2919-2928. 8.R. S. Busk: US patent 4,694,881, 1987. 9.陳俊沐, "鋁合金半固態材料成形技術", 工業材料152期, 88年8月, 155-167. 10.邱正茂, 魏碧玉, "半固態材料成形技術", 中國機械工程學會雙月刊第211期, 85年, 66-77. 11.徐文敏, 彭暄, "半固態鎂合金之射出成形技術", 機械工業雜誌, 86年10月, 141-155. 12.黃東茂, "鎂合金半固態成形技術", 機械工業雜誌, 88年7月, 243-244.. 13.許世昌, "電弧離子鍍膜技術之概述", 工業材料120期, 85年12月, 53-57. 14.鍾長祥, 張嘉珍, "電弧離子鍍膜技術之原理與應用", 工業材料114期, 85年6月, 102-114. 15.林天財, "化學蒸鍍硬質膜技術及其應用", 工業材料143期, 87年11月, 102-113. 16.趙浩勇, 何主亮, 陳克昌, "如何減少陰極電弧電漿沈積薄膜上的微粒", 表面技術雜誌, 第153期, 75-89. 17.Z. F. Zhou, G. M. Tilden, Q. Y. Liu, P. D. Mercer and D. J. Wills, "The Formation and Growth of the Interfacial Alloy Layer in Zn-55%Al-1.5%Si Hot-Dipped Coatings," Galvatech 95, pp. 111-137. 18.R. Shivpuri, Y. L. Chu, K. Venkatesan, J. R. Conrad, K. Sridharan, M. Shamim, R. P. Fetherston, "An evaluation of metallic coatings for erosive wear resistance in die casting applications," Wear, Vol. 192, 1996, PP. 49-55. 19.M. Faccoli, G.M. La Vecchia, R. Roberti, A. Molinari, Proceedings of 27 ° Convegno Nazionale AIM, Orvieto 16-18 Settembre 1998, Vol. 2, AIM Milano, pp. 128. 20.A. Molinari, M. Pellizzari, G. Straffelini, M. Pirovano, "Corrosion behaviour of surface-treated AISI H11 hot work tool steel in molten aluminium alloy," Surface and Coatings Technology, Vol. 126, 2000, pp. 31-38. 21.金重勳, 機械材料, 復文書局, 1996, pp. 453. 22.C. Mitterer, P. H. Mayrhofer, M. Beschliesser, P. Losbichler, P. Warbichler, F. Hofer, P. N. Gibson, W. Gissler, H. Hraby, J. Musil and J. Vlcek, Surf. Coat. Technol. 120-121 (1999) 405. 23.A. Ehrlich, M. Kuhn, F. Richter, W. Hoyer, "Complex characterisation of vacuum arc-deposited chromium nitride thin films," Surface and Coatings Technology, Vol. 76-77, 1995, pp. 280-286. 24.R. R. Aharonov, M. Chhowalla, S. Dhar, R. P. Fontana, "Factors affecting growth defect formation in cathodic arc evaporated coatings," Surface and Coatings Technology, Vol. 82, 1996, pp. 334-343.. 25.J. A. Sue, A. J. Perry, J. Vetter, "Young's modulus and stress of CrN deposited by cathodic vacuum arc evaporation," Surface and Coatings Technology, Vol. 68/69, 1994, pp. 126-130.. 26.R. Gahlin, M. Bromark, P. Hedenqvist, S. Hogmark, Greger Hakansson "Properties of TiN and CrN coatings deposited at low temperature using reactive arc-evaporation," Surface and Coatings Technology, Vol. 76-77, 1995, pp.174-180. 27.Y. Wang, "A Study of PVD Coating and Die Materials for Extended Die-coating Die Life," Surface and Coatings Technology, Vol. 94-95, 1997, pp. 60-63. 28.S. Iwanaga, Y. Sakakibara, T. Konaga, M. Nakamura and T. Kamiya, "Initiation and Propagation of Heat Checking in Aluminum Die Casting Dies," 材料, 第36卷第405號, 1987, pp. 604-609. 29.W. F. Goodwin , "The Solvenite Process vs. Hard Coating," Die casting Engineering Vol. 29, 1985, pp. 75-77. 30.F. J. Diekman, "Laser Bombardment Process for Die Casting Dies," Die casting Engineering Vol. 26, 1982, pp. 24-27. 31.D. S. Rickerby, A. M. Jones and B. A. Bellamy, "X-Ray Diffraction Studies of Physically Vapour-Deposited Coating," Surface and Coatings Technology, Vol. 37, 1989, pp. 111-137. 32.D. S. Rickerby, A. M. Jones and B. A. Bellamy, "Internal Stress in Titanium Nitride Coatings: Modeling of Complex Stress Systems," Surface and Coatings Technology, Vol. 36, 1988, pp. 661-674. 33.彭坤增, 許倍誠, 林招松, 「銅膜鍍鎳層組織及性質受熱潛變之影響」, 中國鋼鐵公司建教合作結案報告, 八十七年十一月. 34.藤井利光, 倉田爭兒, "實施各種表面處理的熱間模具材料之耐鋁熔損性", 模具技術資訊第71期, 2001, 2月, 32-36. 35.K. L. Lin, J. K. Ho, C. S. Jong and J. T. Lee, "Growth Behavior and Corrosion Resistance of 5% Al-Zn Coating," Corrosion, Vol. 49, pp. 759-762.