行政院國家科學委員會專題研究計畫 成果報告

以電化學阻抗分析儀(EIS)及飛行式二次離子質譜儀(ToF-SIMS)對複合式 Zr、Ce 之矽酸鹽綠色防蝕試劑的效能評估研究

研究成果報告(精簡版)

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Using TOF-SIMS and EIS to Evaluate Green Pretreatment Reagents: Corrosion Protection of Aluminum Alloy by Silica/ Zirconium/ Cerium Hybrid Coating

Abstract

The use of chromium (Cr) as an anticorrosion pretreatment ingredient to protect aluminum (Al) alloys is being restricted because of environmental concerns. Our research is under way to find environmentally compliant substitutes for Cr [1, 2]. The effect of silicate surface treatments on the corrosion inhibition characteristics of Al-alloy was studied in 3.5% NaCl. A series of specimens were prepared at different silicate concentrations using different application methods alone or combined with a sealing step in cerium or zirconium solutions. The effect of surface etching was studied. Electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM) and Time of Flight Secondary Ion Mass Spectroscopy (TOF-SIMS) were used to evaluate the corrosion behavior of treated and untreated specimens. Generally, silica/ zirconium/ ceria treatments improved the corrosion resistance due to the formation of protective oxide films which acted as a barrier for oxygen diffusion to the metal surface. Zirconium and cerium sealing specimens showed a superior corrosion resistance indicating that zirconium and cerium played the main role in the passivity mechanism. Based on the EIS and ToF-SIMS results, the performance of silica/ zirconium/ cerium a green pretreatment reagent was successfully evaluated.

Keywords: aluminum(Al)、silicate、cerium、zirconium 、EIS、TOF-SIMS

1. Introduction

Chromate conversion coatings are currently used as a pretreatment for different Al-alloy substrates. This pretreatment provides excellent corrosion protection and good adhesion properties [1]. However, hexavalent chromium Cr(VI) is strongly carcinogenic, and in the future they will be definitely abandoned. Current environmental regulations require the development of environmentally safe pretreatments. Many attempts have been made to find alternatives to chromating such as manganese [2], molybdenum [3], vanadium [4] and cerium [5]. Among these, sol–gel processes can be a potential alternative. Sol–gel processes were initially developed for the deposition of inorganic oxide coatings, but in recent years, the synthesis of organic–inorganic hybrid coatings acquired great importance. These hybrid films show interest because they combine properties of the organic polymeric materials and properties of the ceramics. Hybrid coatings can be prepared over a continuous compositional range from almost organic to almost inorganic [6].

A coating system's electrical resistance is a general indicator of its corrosion protection performance. In this paper, we used electrochemical impedance spectroscopy (EIS) to evaluate the electrical resistance of the coating systems. EIS has proven to be a powerful and convenient technology to

evaluate the performance of coating systems [7]. Static time-of-flight secondary ion mass spectrometry (TOF–SIMS) is extremely useful to investigate the composition and chemical structure of materials surface thanks to its high surface sensitivity (10–20 Å), analytical sensitivity, and direct relation between the chemical composition/structure of surfaces and the fragmentation patterns of TOF–SIMS spectra [8]. In order to examine how well the hybrid films adhered to the Al alloy surfaces, a combination of SEM and TOF-SIMS were conducted in this study.

In this paper, the role of silicate in the corrosion inhibition process would be studied in details at different concentrations and different application. The methods alone or combined with a sealing step in cerium and zirconium solution as a non-chromate coating. The silica/ceria/zirconium (Si/Ce/Zr) hybrid thin films formation process and corrosion resistance were characterized by EIS, SEM and TOF-SIMS.

2. Experimental

2.1 Materials

The aluminum alloy specimens were cut into 10 × 10-mm^2 square panels and mechanically polished by 1200 finish SiC grit paper to a mirror polish (≒ 1μm surface roughness). They were degreased in NaOH (1M), cleaned in oxalic acid (0.1M) and dried in acetone.

The conversion solution contains sodium silicate at different concentration (4 g/L、8 g/L and 16 g/L). Zirconium and cerium solution contains with zirconium tetrachloride and cerium sulfate hydrate respectively at different concentration. The solution pH was adjusted to 2 and 9 with HNO_3 and NaOH respectively. After activation and dry, the specimens were immersed in the mention above solutions for 10 min with agitation. The chemical conversion films that formed on the Al-alloy were dried shortly afterwards at 423 K for 5 min.

2.2 EIS Measurement

Electrochemical impedance spectroscopy (EIS) was used to assess the corrosion protective properties of the hybrid sol–gel pretreatments in a 3.5 mass% NaCl solution which was open to the air during each test and unstirred. EIS data were obtained using EG&G Princeton Applied Research Corp., model 378 electrochemical impedance system which consists of a complete hardware and software package that measures the response of an electrochemical system to a.c. excitation. A three-electrode arrangement was used, consisting of a saturated calomel reference electrode, a platinum foil as counter electrode and the exposed sample as working electrode. The working area was 1.0 cm^2. All the measurements were carried out at room temperature in a Faraday cage. The measurement conditions were an amplitude voltage of 10 mV, a frequency range of 0-50 Hz and a solution temperature of 303 K.

2.3 TOF-SIMS analysis

The surfaces of coated films were observed by SEM and TOF-SIMS. The TOF-SIMS data were recorded on a TOF-SIMS IV instrument (ION-TOF GmbH, Germany) which located in National Tsing-Hua University, Taiwan. In the TOF-SIMS, a focused primary ion beam of 25 keV Ga^+ ions was used at a current of typically 0.5-1 pA. and with a 20-100 ns pulse width, oriented 45^o to the sample. The data were recorded by

scanning the primary ion beam over an analysis area (50×50 μm^2 to100×100 μm^2) and storing the results in a raw data file for retrospective extraction of selected ion images and of spectra from the selected areas within the analysis area. Data of high-resolution mass spectra ($m/\Delta m$ = 2000-5000; lateral resolution, 3-4 μm) and high lateral resolution images (lateral resolution 0.5 μm, $m/\Delta m$ = 200-1000) was recorded separately, to ensure that the accumulated ion dose at the molecular imprint is kept below the so-called static limit, 1×10^{13} ions/cm^2.

3. Results and discussion

The corrosion protection performance will be affected by several factors. For example: concentration of sodium silicate, zirconium tetrachloride and cerium sulfate hydrate. Besides, pH value of solution and the structure of thin film also affect the corrosion protection performance. According to EIS results (Fig. 1), the best corrosion resistance was obtained using the concentrations which are listed in following: (1) sodium silicate concentration is 8g/L (2) zirconium tetrachloride is added 0.25 g (3) cerium sulfate hydrate concentration is 1000ppm. The more concentrated (16 g/L) sodium silicate solution affects negatively the corrosion resistance. This may be due to the formation of a rigid glassy-like layer of silicates which can favor the propagation of cracks through which the localized corrosion takes place. Moreover, the corrosion protective layer is considered to be a sequential process with breakdown of the individual oxide/silicate and oxide layers by the action of chloride and initially also hydroxide released from the silicate seal. Fig. 2 shows that the specimens passed with zirconium tetrachloride treatment before cerium sulfate hydrate under pH=9 has a better corrosion resistance performance. The results confirm that the sealing effect zirconium is better than cerium.

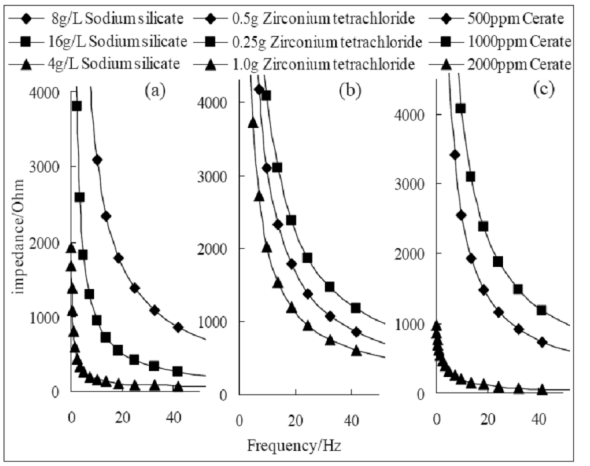

Fig. 1.Concentration effect of sodium silicate, zirconium tetrachloride and cerium sulfate hydrate

The surface morphology was studied with SEM which is showed in Fig. 3. Moreover, the distribution of zirconium and cerium oxides over the pitting areas is more uniform and adequately covered the specimen. Finally, TOF-SIM spectrum also showed the surface chemistry of the specimen which is showed in Fig. 4 and Fig. 5. Through the TOF-SIMS spectrum and image could confirm the thin film composition.

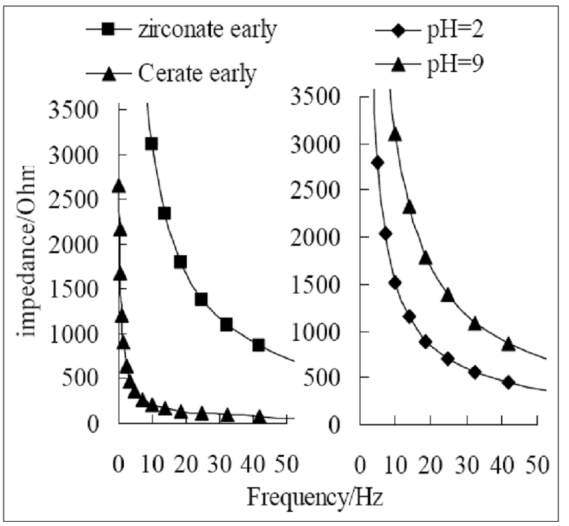

Fig. 2 sequence process and pH effect of zirconium tetrachloride and cerium sulfate hydrate

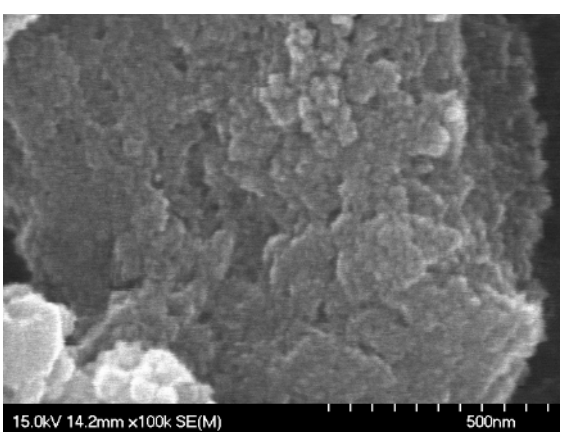

Fig. 3 SEM image for coating specimen

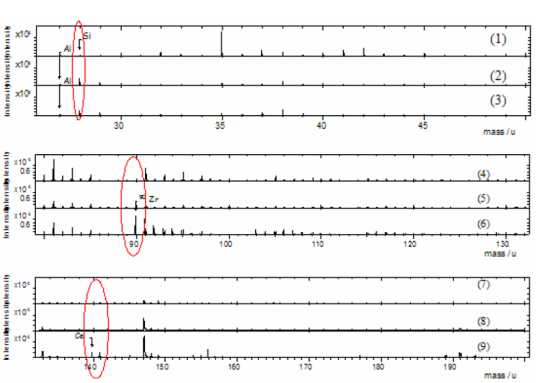

Fig. 4 TOF-SIMS static spectrum for three layers coating specimen

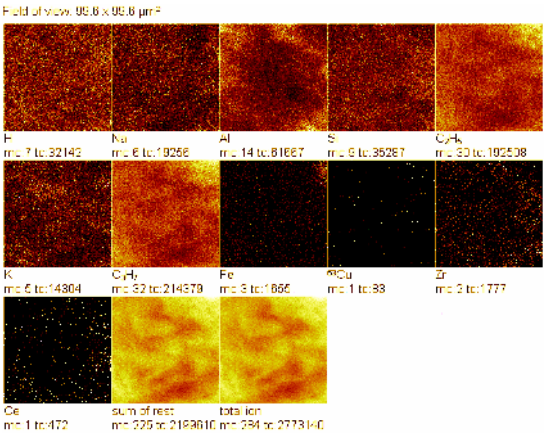

Fig. 5 TOF-SIMS image spectrum for three layers coating specimen

4. Conclusions

In the present work a hybrid green pretreatment reagents Si/Zr/Ce have been deposited on Al-alloy. The surface chemistry of the samples was investigated with EIS and TOF-SIMS. The surface morphology was studied with SEM. The following conclusions can be drawn from results presented here:

The present work shows that hybrid sol-gel Si/Zr/Ce coatings provide corrosion protection and may be used as alternative candidates for pretreatments for aluminum alloys. The properties of the hybrid sol-gel coatings are strongly dependent on the preparation conditions and sequential process. During the corrosion protection films formed, and cerium can incorporate into the pores of silicate oxide thick film to form a high corrosion resistant layer. After specimens immered in silicate solution, treated specimens in zirconium before cerium have better corrosion protection performance than cerium before zirconium.

5. Acknowledge

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under project (NSC95-2113-M-040-005) is acknowledged. We thank professor Y. C. Ling (GM Lab in NTHU) for assistance in collecting ToF-SIMS data.

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行政院國家科學委員會補助國內專家學者出席國際學術會議報告

96 年 06 月 27 日

附件三

報告人姓名	麥富德	服務機構及職稱	中山醫學大學 助理教授
會議時間地點	96 年 06 月 03 日至 07 日 中國大陸大連	本會核定補助文號	NSC 95-2113-M-040-005
會議名稱	(中文) 第 **30** 屆國際毛細管層析分析化學（**30th ISCC**）研討會 (英文) **30th International Symposium on Capillary Chromatography**		
發表論文題目	(中文) (英文) **A Study of Competitive Adsorption and Photodegradation of Five Triphenylmethane Dyes at Same Time from Aqueous on Nano-TiO2 Suspensions**		

報告內容應包括下列各項：

一、參加會議經過

此次與國內學者由中興大學教務長鄭政峰教授組團前往大連星海會議暨展示中心參加由大陸中科院大連化物所舉辦的第 30 屆國際毛細管層析分析化學研討會(六月三日至六月七日)。參與研討會之學者來自世界各地，除中國大陸外，有香港、澳門、新加波、美國、加拿大、日本、英國、荷蘭、德國及臺灣等國家及地區。來自世界各地的學者於會中以口頭報告或壁報方式發表最近的研究成果，與參與者共同討論。臺灣此次去參加的國內學者共有七位，另外有四位碩博士班的學生與會。本人於會中以 "**A Study of Competitive Adsorption and Photodegradation of Five Triphenylmethane Dyes at Same Time from Aqueous on Nano-TiO2 Suspensions**"為題於大會發表。

二、與會心得

在研討會過程中發現分析化學學者的研究是與世界的潮流接軌的，也是走在世界科技前鋒，相信未來國際分析化學領域將是蓬勃發展。從研討會中亦感到化學分析技術研究之多元化，國內學者的研究稍偏重於分析方法的開發，對於硬體方面之研究較少著墨。反觀大陸學者的研究，由於經費的大量挹注及研究成果獎勵下，不論是在分析技術或硬體的研究上均有極大的進步，此可由大陸製造儀器設備廠加大量增加可以看出。每次參加國際學術研討會，都能見識國際化學分析技術研究之進展，激發起努力研究之方向與動力。

三、考察參觀活動(無是項活動者省略)

研討會亦安排參觀中科院大連化物所，由於為新建築，不管是儀器或設備均為世界一流。而年輕學者之工作態度與士氣，都會讓人擔心台灣年青一代未來之競爭力在那裡。也參觀了中草藥研究開發組，設備、技術、進度、效率等都很值得我們學習。

四、建議

國內學者的研究稍偏重於分析方法的開發，對於硬體方面之研究較少著墨，此方面建議國科會應鼓勵國內學者朝此方向努力。

五、攜回資料名稱及內容

會議手冊一本，內容包含演講與海報之摘要。

表 Y04

A Study of Competitive Adsorption and Photodegradation of Five Triphenylmethane Dyes at Same Time from Aqueous on Nano-TiO_2 Suspensions

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KEY WORDS:

TiO_2, Photodegradation, Triphenylmethane, Dye, Adsorption

ABSTRACT

Recent developments of advanced oxidation processes (AOPs), have led to new improvements of the oxidative degradation of the organic compounds. While most photocatalytic studies have used anatase TiO_2 as photocatalyst for single model compound, numerous studies have been carried out to evaluate the potentiality of TiO_2. Among others, several dyes appear as a model compound at same time for degradation of dye in aqueous system. In this work, a completive photodegradation study of the triarylmethane dyes is reported in aqueous TiO_2 suspensions. The effect of various adsorbed dye in TiO_2 aqueous suspension was studied.

The adsorption and photodegradation have been investigated in illuminated TiO_2 suspension for five dyes, including cationic dyes, Crystal Violet (CV), Ethyl Violet (EV), Malachite Green (MG), Brilliant Green (BG), and an anionic dye, Sulfan Blue (SB). Our results indicate that factors such as, UV illumination, pH value of the aqueous solution, concentration of TiO_2, and salt addition, all determine the rate of photodegradation. The photocatalytic activities of adsorbed dyes prepared under different pH values were examined that on the positively charged TiO_2 particle surface by a sulfonate group, anionic dye (SB) has better degradation rate. On the other hand, on the negatively charged TiO_2 particle surface, cationic dyes (CV, EV, MG, and BG) have better degradation rate by a dialkylamino group. The cationic dye including di-ethylamino groups have better degradation rate

than the cationic dye including dimethylamino groups (EV>CV; BG>MG) at different pH values. When addition salt under acid aqueous solution, most of the five dyes tends to positive effect, but under base aqueous solution, they tend to negative effect. For photodegradation of dyes, the degradation rate were proposed and discussed in this research.