Advanced Materials Research Vols. 399-401 (2012) pp 390-393
Online available since 2011/Nov/22 at www.scientific.net

doi:10.4028/www.scientific.net/AMR.399-401.390

Research of Aluminum Sheet Encapsulated by Organic Silane Acrylate Resin and Tetraethyl Orthosilicate

GAO Ai Huan[1,a], PI Pi Hui[2,b], CHENG Jiang[2,c] ,YANG Zhuo Ru[2,d]

[1]School of Chemistry and Chemical Engineering, Zhao Qing University, China

Donggang, Duanzhou District, Zhaoqing, 526061,Guangdong, China

[2]School of Chemistry and Chemical Engineering, South China University of Technology, China

No. 381, Wushan Road, Tianhe District,Guangzhou, 510640, China

[a]gaoah@zqu.edu.cn, [b]phpi@scut.edu.cn, [c]cejcheng@scut.edu.cn, [d]zhryang@scut.edu.cn

Keywords: organic-inorganic hybrid; organic silane acrylate resin;sol-gel; aluminum sheet

Abstract: Aluminum sheet was encapsulated by inorganic-organic hybrid film through a base catalyzed sol-gel method using organic acrylate silane resin PMBV and TEOS as precursors. FTIR and AFM characterizations prove that PMBV and TEOS have hydrolyzed and co-condensed with each other in the sol-gel process to form an uniform film on the surface of aluminum sheet. XPS result shows hydroxyl groups on aluminum surface have taken part in the co-condensation reaction.

Introduction

Organic silane acrylate resin is a kind of acrylic ester polymer containing siloxane groups. It is widely used to prepare organic-inorganic hybrid material or to form thin film on the surface of material[1]. The thin film formed on the surface of metal through sol-gel process using organic silane acrylate resin as the precursor can not only protect metal from corrosive medium, but also promote the compatibility of metal with organic system.

In this paper, organic silane acyrlate resin Poly (Methyl methacryalte-n-Butyl acrylate-Vinyl trieth oxysilane (PMBV) and tetraethyl orthosilicate (TEOS) were used as co-precursors to encapsulate aluminum with organic-inorganic hybrid film via sol-gel method using ethanol/H_2O as dispersion media. Fourier transformation infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) analysis and atomic force microscopy (AFM) were used to character the hydrosis-condensation product of co-precursors and the encapsulated aluminum sheet.

Experimental

Materials

Organic silane acrylate resin PMBV is polymerized by ourselves（the molecular weigh is 3700 and the content of silane is 3.89%）. Dimethylbenzene, ethanol and ammonia are all analytical reagent available on market.

Encapsulation

An aluminum sheet with the size of length 5 cm, width 5 cm and thickness 0.5 mm was hang from the muddle after ultrasonic cleaning. The muddle was fitted to a three neck-round bottom flask with 50 mL ethanol. Then the ethanol was heated to 60 °C under stirring. A mixture of 3 g PMBV (dissolved in 10 mL dimethylbenzene), 2 mL TEOS and 30 mL ethanol and another mixture of 3 mL ammonia, 5 mL distilled water and 30 mL ethanol were added drop-by-drop over 1 hour into the flask simultaneously. The mixing solution was further stirred for 6 hours and then the aluminum sheet was taken out before gel formed to be dried at 80 °C for 24 hours. The gel formed was then dried to be charactered.

Characterization

Infrared absorption spectra of gel were recorded by using a Fourier transition infrared spectrometer Vector 33 (FTIR, Bruker Co.). The surface analysis of the aluminum sheet was performed using Atomic force microscope (AFM, CSPM5000, Ben Yuan Co.) and X-ray Photoelectron Spectroscopy (XPS, Axis Ultra DLD, Kratos Co.).

Results and discussion

Encapsulation process

In the sol-gel process, the ethoxy groups of precursors hydrolyze and then self-condense or co-condense in the ethanol/water media under catalysis by the ammonia solution. The organic-inorganic hybrid material is just formed by the co-condensation of the hydrosis products of different precursors.

There is a layer of aluminum oxide on the surface of aluminum sheet due to their exposure to the air [2].The surface of the aluminum oxide layer in a humid or moist environment has a significant population of hydroxyl groups. These surface hydroxyls can participate in the sol–gel condensation reaction of the TEOS and PMBV to form a chemical linkage, Si–O–Al, between the aluminum and the silicon sol–gel film [3]. This chemical bond formation produces the strong interaction of the organic-inorganic hybrid layer with the aluminum surface.

FTIR analysis

Fig. 1 gives the FTIR spectra of the hydrolysis-co-condensation product of PMBV and TEOS. The absorption peak near 1730 cm^{-1} is due to the stretching vibration of carbonyl group. The peak appeared near 2940 cm^{-1} is assigned to methyl and methylene group. Those groups are all come from PMBV. it shows that PMBV has taken part in hydrolysis-condensation. Peaks near 1170 cm^{-1} and 790 cm^{-1} are both attributed to the vibration of Si-O-Si group. The peak near 950 cm^{-1} shows the exit of Si-OH group in gel. Those three peaks demonstrate the exitence of SiO_2 in the product of hydrolysis-co-condensation [4]. The analysis proves that PMBV and TEOS have hydrolyzed and co-condensed with each other in the sol-gel process.

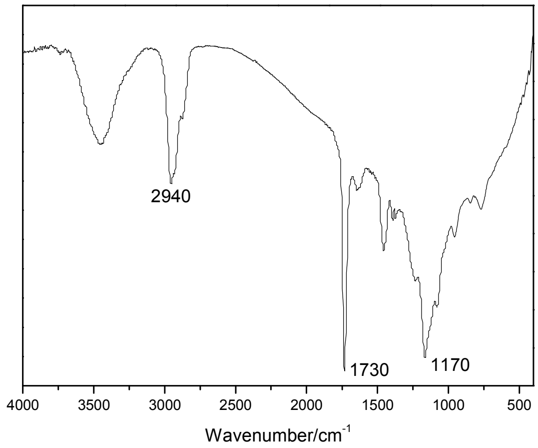

Fig.1 FTIR spectra of the product of hydrolysis-co-condensation of PMBV and TEOS

AFM analysis of encapsulated aluminum

AFM was employed to observed the surface morphology of a encapsulated aluminum made at 60°C and in the condition as follows: the amounts of PMBV, TEOS, ammonia and water are 3.0g, 2.0mL, 3mL and 3mL，respectively. It can that be seen from Fig. 2 the surface of encapsulated aluminum is smoothly and uniformly. The result means TEOS and PMBV have hydrolyzed and co-condensed with the –OH groups on the surface of aluminum to form an organic-inorganic hybrid films on the surface of aluminum sheet.

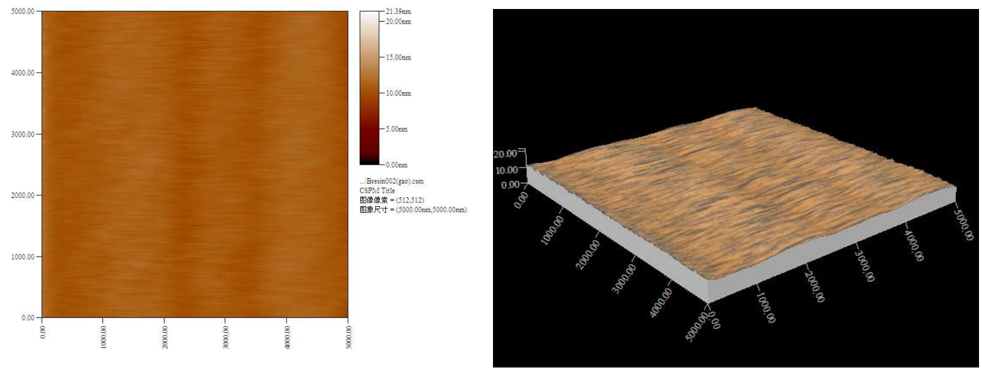

Fig. 2 AFM images of encapsulated aluminum surface

XPS analysis of encapsulated aluminum

To confirm the existence of sol-gel film on the surface of aluminum sheet, angle-dependent XPS measurement was performed. Full spectra obtained at various take-off angles of 15°, 60° and 90° are similar to each. The characteristic peaks of Si 2s (102.0 eV) and Si 2p (153.0 eV) manifest that the presence of Si element on the surface of the particles is evident, suggesting TEOS and VTES have been successfully bonded onto the surface of aluminum sheet. The signals at 285.0 eV (C1s) and 532.0 eV (O1s) with binding energy reveal that there are C and O elements on the surface of encapsulated aluminum sheet. No signal appears near 73.3eV（Al 2p）and 116.3eV (Al 2s), indicating the depth of encapsulated film is more than 10nm. For the XPS measurement can just analyze elements on the surface of material in a depth of no more than 10 nm.

The quantitative evaluation of the XPS spectra was carried out by determining the areas of the Si2p,C1s and O1s peaks and multiplying them to obtain the appropriate sensitivity factors. The results are given in Table 1. As can be seen from Table 1, the contents of three elements change with the change of take-off angle. The contents of Si element are 4.51%, 4.70% and 4.81% for take-off angles of 15°, 60° and 90°, respectively. The result indicates that the content of Si increases with the depth into the encapsulated film. It maybe cause by condensation reaction of hydroxyl groups on aluminum surface with the hydrosis product of PMBV and TEOS.

Table1 XPS data for the surface of encapsulated aluminum sheet

Take-off angle（°）	Elemental contents/%		
	C	O	Si
15	75.20	20.29	4.51
60	75.40	19.91	4.70
90	76.06	19.13	4.81

Conclusions

The inorganic-organic hybrid film encapsulated aluminum sheet was prepared by a base catalyzed sol-gel method using organic acrylate silane resin PMBV and TEOS as precursors. FTIR and AFM characterizations prove that PMBV and TEOS have hydrolyzed and co-condensed with each other in the sol-gel process to form uniform film on the surface of aluminum sheet. XPS result shows hydroxyl groups on aluminum surface have taken part in the co-condensation reaction as the hydrosis product of PMBV and TEOS.

Acknowledgments

The work has been financially supported by projects of the Natural Science Foundation of China (20976059), the Fundamental Research Funds for the Central Universities (2009ZM0141) and the Guangdong Provincial Natural Science Foundation of China (07006528). The authors are grateful for K. Chen (for FTIR) and H. Yang (for AFM) for their experimental and measurement contributions.

References

1. Jones R G, Ando W, Chojnowski J, et al. Silicon-Containing Polyners-The Science and Technology of Their Synthesis and Applications[M]. Ntherlands, Kluwer Academic Publishers, 2000, p: 582-588.

2. Karlsson P, Palmqvist AEC, Holmberg K. Surface Modification for Aluminum Pigment Inhibited. Advance in Colloid Interface Science 2006; 128-130:121-134.

3. Li L J, Pi P H, Wen X F. Aluminum Pigments Encapsulated by Inorganic–organic Hybrid Coatings and their Stability in Alkaline Aqueous Media. Journal of Coating Technology Research 2008; 5: 77-83

4. Li L J, Pi P H, Wen X F, et al. Optimization of sol-gel coatings on the surface of aluminum pigments for corrosion protection [J]. Corrosion Science, 2008, 50, 795-803.