

Sol-Gel-Derived Alumina/Polyvinylpyrrolidone Hybrid Nanocomposite Film on Metal for Corrosion Resistance

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ABSTRACT: With the addition of polyvinylpyrrolidone (PVP), alumina sol with an aluminum *sec*-butoxide/water molar ratio of 1 : 45 was synthesized. The surface tension of this alumina sol was found to be lower by 35% than the sol without PVP. Alumina/PVP hybrid film with a critical thickness up to 2 μm was fabricated by dip-coating method. The heat treatment between 200 and 300°C could produce a film with perfect hybrid nanocomposite structures. Alumina particles with a size of about 20 nm were uniformly distributed in this material. The hardness of the film samples increased with the increment of heat treatment temperature, and hardness values higher than the

original metal were detected after heat treated above 400°C. The film-coated metals that were heat treated below 150°C or above 400°C exhibited relatively weak adhesion, but strong adhesion was obtained when heat treated between 200 and 300°C for 30 min. The corrosion rate of the film-coated metal that was heat treated between 200°C and 300°C for 30 min was lower by 95% than the uncoated metal. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 105: 697–705, 2007

Key words: corrosion resistance; alumina; hybrid nanocomposite film; polyvinylpyrrolidone; sol-gel

INTRODUCTION

Ceramic coatings are usually deposited on metals for improving their performances in high-temperature aggressive environments.¹ Low temperature applications are also important, where the coatings provide corrosion resistance or good dielectric properties.²

There are several methods for depositing ceramic coatings, including plasma-spray, anodic oxidation, physical vapor deposition, electrophoresis, and sol-gel deposition.^{3–7} The deposition of sol-gel coatings to improve the corrosion resistance of metals represents numerous advantages including the simplicity of the deposition methods, the chemical bonding of coating to substrate resulting in high adherence and chemical stability, and the low sintering temperature.^{8,9} These characteristics are related to the good corrosion resistance of coated specimens.^{10–15}

However, there are limits of sol-gel application to coating of metals. Major drawbacks of sol-gel processing for coating metals are crackability and thickness limits. Sometimes also the thermal treatment may be critical.^{16,17} They may affect several properties and may be deleterious in wet corrosive media.

Cracks are due to stresses developing during drying and thermal treatment. Stresses in sol-gel derived films are due to shrinkage and thermal expansion mismatches. Tensile stresses develop during drying, and can lead to crack formation if the film is thicker than a critical value.^{18,19} It was identified by Kozuka et al. that the critical thickness achievable via single-step deposition is often below 0.1 μm for nonsilicate-oxide films.²⁰ However, for many applications, like thermal barriers, protection from highly corrosive media, thick layers are usually required.²¹ Sol-gel derived organic-inorganic hybrid nanocomposite protective coatings have attracted great attention recently because they can effectively overcome the major drawbacks mentioned earlier.^{22,23} Hybrid SiO_2 and ZrO_2 coatings were examined to be able to provide excellent corrosion resistance to metal surface.^{24,25} This work aims at investigating an Al_2O_3 /polyvinylpyrrolidone (PVP) hybrid nanocomposite film for corrosion resistance. Aluminum *sec*-butoxide (ASB) has been widely selected as the precursor of Al_2O_3 .^{26–28} Generally the molar ratio of ASB to water was fixed around 1 : 100 to obtain a sol with an acceptable lifetime.^{29–31} However, due to the low Al_2O_3 content, the thickness of the film prepared from this sol is usually below 0.1 μm . The present article describes the synthesis of an alumina sol with an ASB/water molar ratio of 1 : 45 and the fabrication of compact, crack-free Al_2O_3 /PVP hybrid nanocomposite film with a thickness up to 2 μm on metallic substrates. The effects of heat treatment on the

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hardness, adhesion, thickness, and corrosion resistance of coated samples were investigated.

EXPERIMENTAL

All chemicals were used as received without further purification. ASB (98%) was purchased from Chemat Technology, Inc. (Northridge, CA). Because ASB is so moisture sensitive that it will rapidly transform into white Al_2O_3 powders if exposed to the air, it should be carefully kept. PVP (K90, average molecular weight: 630,000, 95%) was obtained from Boai Friends Union Chemicals Co., Ltd. (Jincheng, China). Nitric acid (65%) was purchased from Shanghai Jiachuan Chemicals Co., Ltd. (Shanghai, China).

Initially, deionized water was heated in a glass beaker until it reached 80°C . ASB was added by syringe to the water with continuous mixing. The molar ratio of ASB to water was 1 : 45. As hydrolysis took place, a large number of white Al_2O_3 precipitates were immediately produced in the solution, and the temperature of the solution rose to 90°C , at which it was maintained for 4 min. After stirring for 4 min, nitric acid was added into the solution stepwise with stirring until it was transformed into a transparent solution. Then, PVP was added to the mixture solution according to an amount of 100 mg PVP per mL solution, followed by drastically stirring for further 60 min. The pH value of the as-synthesized sol was examined to be about 4. For comparison, alumina sols with ASB/ H_2O molar ratios of 1 : 100 and 1 : 45 were also synthesized through the same process, as described earlier, but without PVP addition.

The substrates used in this study were steel plates. The individual plates were cut from a single sheet, and then ground and polished, to yield a flat, mirror-like surface. The polished plates were ultrasonically cleaned in acetone for 15 min and deionized water for an additional 15 min. The clean substrates were dried at 50°C for 30 min and then cooled to ambient temperature in air, prior to coating. Alumina-gel film samples with or without PVP were scraped off the substrate and served for differential thermal analysis (DTA).

The dip-coating was performed at ambient temperature and pressure, in a "clean-room" environment. Each substrate was immersed into the sol reservoir and allowed soaking for 30 s. The coated substrate was then removed from the bath at controlled rates from 3 to 18 cm min^{-1} . The substrate was then dried at room temperature for 24 h, followed by heat treatment at various temperatures within $50\text{--}600^\circ\text{C}$ for 30 min.

The viscosity of the sols was measured at room temperature using a Brookfield DV-II+ Viscometer.

Gel films were examined using DTA and thermogravimetric analysis (TGA) (NETZSCH STA 449C), using a heating rate of $10^\circ\text{C min}^{-1}$ in air. The temperature range is from room temperature to 600°C . The gel films were scraped off the substrate and served as the sample. The surface tension of the coating solutions was measured using a surface tension meter (CA-XP150). The cross section morphology of the thick (1.5 mm) alumina/PVP gel film was observed by a field-emission scanning electron microscope (A JSM-6700F). The thickness of the films was determined using an ellipsometer (GAERTNER, L116C). The Micro Vickers Hardness of the specimens was measured using a Vickers Hardness Tester (HXD-1000TMC). Adhesion was measured by tape test using ASTM D 3359. A lattice pattern with 11 cuts in each direction is made in the film to the substrate, pressure-sensitive tape over the lattice and then removed, and adhesion is evaluated by comparison with descriptions. The corrosion rates of metallic samples coated with alumina or alumina/PVP hybrid film were evaluated by the ferric chloride test, according to Chinese Industrial Standard, GB 4334.7-84. The corrosion rate is defined as the weight loss per unit surface area per unit time after holding a coated specimen in 6% ferric chloride solution at 35°C for 24 h. The corrosion rates are calculated relative to the corrosion rate of the uncoated metallic substrate as 100%. The optical micrographs of coated and uncoated metal samples were taken using a Metal Microscope Image Analysis Instrument (HXD-1000TM).

RESULTS AND DISCUSSION

Effects of PVP addition on the oxide concentration and viscosity of alumina sols

As we know, the oxide concentration and viscosity of a coating solution have great influence on the thickness and quality of films prepared by dip-coating operation. For the preparation of thick film material, it is necessary to obtain a coating solution with high oxide concentration. In this work, the oxide concentration of the alumina sol was proportional to the ASB/water molar ratio. It was found that the gelation time of the alumina sol without PVP was greatly shortened with the increment of the ASB/water molar ratio. The sol with an ASB/ H_2O molar ratio of 1 : 100 did not gel within 200 h, but the sol with an ASB/ H_2O molar ratio of 1 : 45 gelled 2 h later. With the addition of PVP, the gelation time of the sol with an ASB/ H_2O molar ratio of 1 : 45 was found to be prolonged up to 100 h.

Besides gelation time, the change in viscosity of a sol with sol aging time is another initial indicator of the suitability of a particular sol for coating.²¹ A sol exhibiting an excessive high or low viscosity value is

not suitable for producing thick, homogenous coating film by dip-coating operation. Due to excessively low viscosity, very little amount of sol can adhere to the substrate during dip-coating operation contributing little to thickness deposition. On the contrary, a sol with pretty high viscosity is prone to produce an excessively thick gel film, leading often to formation of cracks during heat treatment. The time dependence of viscosity of as-synthesized alumina sols is shown in Figure 1. It can be seen the viscosity of the alumina sol with PVP (ASB/H₂O molar ratio = 1 : 45) could remain about 30 mPa s within 100 h. A stable sol with a viscosity value of 32 ± 4 mPa s has been found to be much favorable for producing crack-free, continuous coating material.²¹ Therefore, the alumina sol with PVP could well satisfy the oxide concentration and viscosity requirements for the preparation of thick alumina film by dip-coating method.

Densification of alumina/PVP hybrid film

Figure 2 shows the DTA-TGA curves of alumina-gel film samples without [Fig. 2(a)] or with [Fig. 2(b)] PVP and pure PVP sample. Because ASB is extremely moisture sensitive and in this work ASB reacted directly with excessive water (the ASB/water molar ratio is 1 : 45), the as-synthesized alumina gels contained very few ASB molecules. The alumina gel without PVP exhibited a sharp endothermic peak at 103°C due to the evaporation of water solvent. An exothermic peak was observed in the DTA curve at 308°C due to decomposition of residual organic groups in the gel. Therefore, the weight loss occurred below 150°C was mainly caused by the evaporation of the solvent, whereas the weight loss occurred within the temperature range from 200 to 400°C was mainly caused by the decomposition of

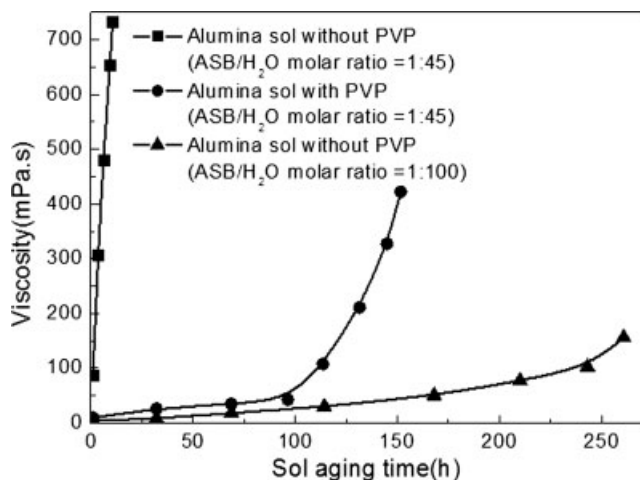


Figure 1 Changes in viscosity of alumina sols with sol aging time.

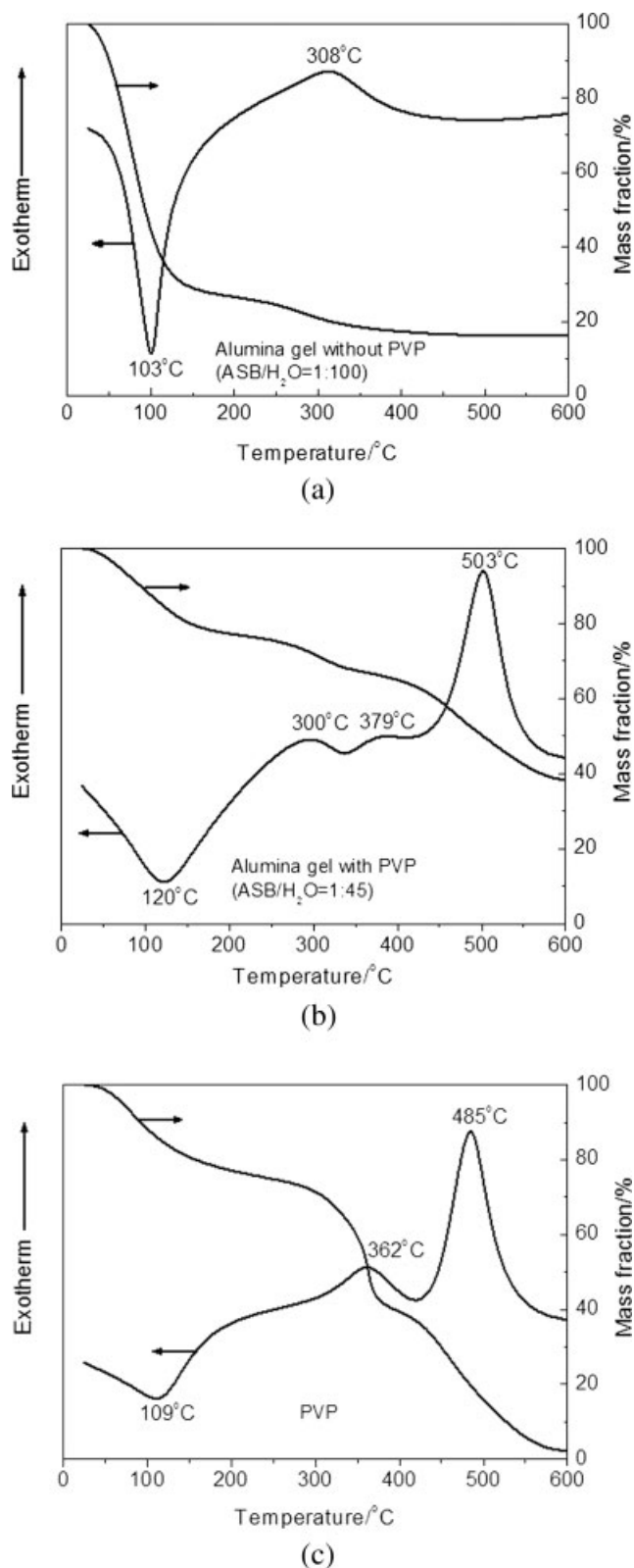


Figure 2 DTA-TGA curves of alumina gel without PVP (a), alumina gel with PVP (b), and pure PVP (c).

the organic groups in the gel. No exothermal peak and little mass loss were detected at a temperature above 400°C, implying the organic compounds were

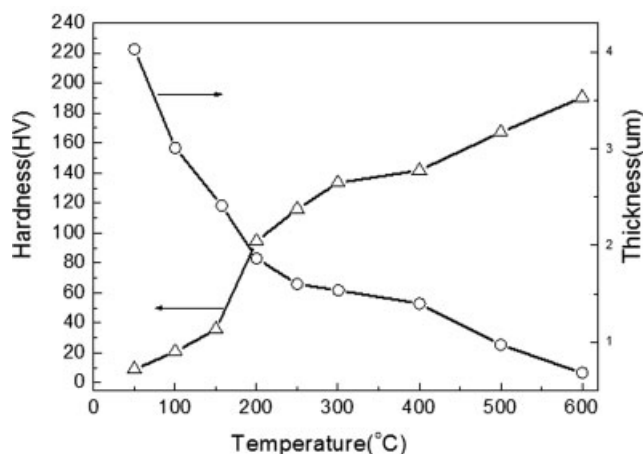


Figure 3 Hardness and film thickness of alumina/PVP hybrid film samples plotted against heat treatment temperature.

burnout before 400°C. When PVP was added, the evaporation of water solvents produced a low, wide endothermic peak centralized at 120°C, indicating the water solvents escaped gradually from this gel material. The organic compounds were decomposed progressively within a wide temperature range from 200 to 600°C. The exothermic peak at 300°C was mainly caused by the decomposition of butyl alcohol molecules resulting from the hydrolysis of ASB. The exothermic peak at 379°C corresponded mainly to the burning of few residual butyl alcohols and the decomposition of some organic groups of PVP molecules. There was a sharp exothermic peak at 503°C accompanying great mass loss that was believed to be assigned to the burning of the carbon chains of PVP molecules. The thermal behavior of pure PVP is a little bit similar to that of the alumina/PVP film sample, but two different points can still be clearly seen, namely the burning of PVP chains in pure PVP sample occurred at 485°C and the total mass loss approaches zero. Based on earlier discussion, three conclusions can be concluded. Firstly, the densification of the alumina/PVP hybrid gel material was much more retarded than the alumina gel without PVP. Secondly, the burning of PVP chains in alumina/PVP sample was much more retarded than the pure PVP sample due to the interaction between PVP and alumina particles. Thirdly, to obtain a film with intact alumina/PVP hybrid structures, it is necessary to control the heat treatment temperatures within 200–300°C.

In this work, alumina gel films were prepared from alumina sols with or without PVP by same dip-coating operation. The alumina/PVP hybrid film was found showing excellent anticracking ability, whereas cracks were invariably observed in the alumina gel film without PVP. The PVP has been used

as an effective agent to suppress the cracking in the thick ferroelectric $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ film.³² It is currently agreed that the addition of PVP can suppress the cracking because it can retard the densification of some sol-gel materials. We have determined in this work that the alumina sols without or with PVP had surface tension values of 78.3 and 51.1 mN m^{-1} , respectively. The surface tension of a PVP-water solution with a same PVP content to the alumina sol with PVP was measured to be 47.5 N m^{-1} , implying the addition of PVP was indeed effective to decrease the surface tension of water or alumina sol without PVP. The authors believed the low surface tension of the sol with PVP made also contribution to the anticracking effect of PVP. Cracks in sol-gel materials are mainly caused by the effect of capillary pressure. According to the Laplace's law, the liquid inside the pores exerts a stress on the "walls" of the capillaries during drying, which is inversely proportional to the pore diameter but proportional to the surface tension of the liquid.³³ Therefore, the liquid with a lower surface tension inside a bigger pore will produce a smaller stress on the "walls" of the capillaries during drying. The retarded densification of the alumina gel with PVP could prevent the production of very small capillaries during the early period of heat treatment. Furthermore, the surface tension of this sol was lower by 34.7% than the sol without PVP. So, excessive high capillary pressure was avoided, resulting in thick, crack-free alumina/PVP hybrid gel film. The critical thickness of this alumina/PVP hybrid film was examined to be about 2 μm , which was about 16 times higher than the alumina gel film without PVP.

Figure 3 gives the changes in hardness and thickness of alumina/PVP hybrid film samples with the

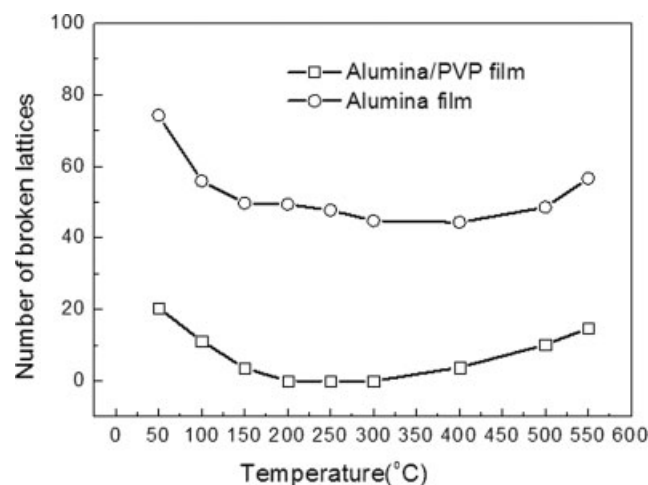


Figure 4 The number of broken lattices recorded during the adhesion test plotted against the heat treatment temperature.

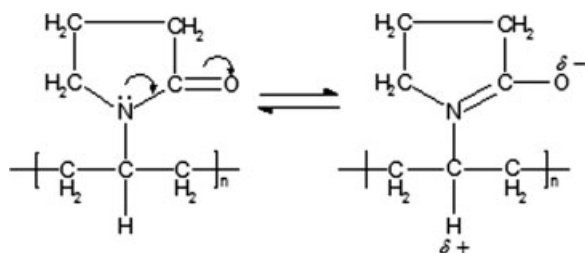


Figure 5 Schematic mesomeric structures of PVP.

heat treatment temperature (the heat treatment time was 30 min). The film thickness was gradually decreased from 4 to 0.7 μm when the heat treatment temperature was increased from 50 to 600°C confirming the densification progressed within a wide temperature range. There were two temperature ranges in which the thickness decreased relatively fast. One was from 50 to 200°C, the other was from 400 to 600°C. Obviously, these two fast decreases in thickness corresponded to the evaporation of water solvents and the burning of PVP, respectively. Accordingly, the hardness was kept increasing within the whole temperature range. Rather rapid increase in hardness was also detected within the temperature ranges from 50 to 200°C and 400 to 600°C. For comparison, the hardness of the original metal was also measured. This substrate was polished and cleaned before served for hardness measurement. The coated sample heat treated at 500°C exhibited a hardness value higher by 7% than the original metal, whereas an increment of 24% was confirmed for the sample heat treated at 600°C. Obviously, the fast enhancement of hardness is due to the formation of Al₂O₃ films with the burning out of PVP at 500 or 600°C. The coated samples heated between 300 and 400°C exhibited comparable hardness with the original metal. The hardness of the coated sample heated at 250°C for 30 min was only lower by 24% than the original metal, implying the heat treatment between 200 and 300°C could sufficiently densify the alumina/PVP hybrid film. Relatively low hardness values were detected when the samples were heat treated below 150°C. We assigned

this to the fact that PVP cannot be cross-linked below 160°C.

Effect of heat treatment on the antibreaking ability of coating film on metal during adhesion test

Figure 4 indicates the number of broken lattices recorded during the adhesion test plotted against the heat treatment temperature. According to the cross-cut tape test method (ASTM D 3359), a lattice pattern with 11 cuts in each direction was made in the film to the substrate. The number of broken lattices due to removal of an adhesive tape was counted. Because a total of 100 lattices were examined, the number of the broken lattices also represents the percentage area where flaking occurs due to removal of an adhesive tape. The results are generally classified as follows: 0B ($\geq 65\%$), 1B (35–65%), 2B (15–35%), 3B (5–15%), 4B ($\leq 5\%$), and 5B (0% or none). According to Figure 4, the alumina gel films without PVP heat treated between 50 and 550°C were easily broken by removal of an adhesive tape. The cracks and weak interface bonding between film and metal would probably be responsible for this phenomenon. With the addition of PVP, the antibreaking ability of the film-coated metal was greatly enhanced. A good level of adhesion (5B) was achieved in the samples that were heat treated between 200 and 300°C.

Actually, in last decade, PVP has kept attracting great attention in the field of colloid and interface science because it was found that various stable oxide or metal colloids could be obtained with PVP addition.^{34–38} It is generally agreed that PVP exhibits mesomeric structures (see Fig. 5).^{35,39,40} These structures make it possible for PVP molecules to form hydrogen bond or coordination linkage with various oxides or metals. There have been many researches on the interaction of PVP with oxides or metals.^{38–43} Israel et al. have demonstrated that the C=O group of the PVP and the surface —OH group of Al₂O₃ colloidal particles form a hydrogen bond (see Fig. 6).³⁹ Similar interaction between PVP and TiO₂ particles was confirmed by Sato et al.⁴³ It was reported that PVP can form coordination compounds with a wide variety of metals (Fe, Mn, Co, Zn, and Ni

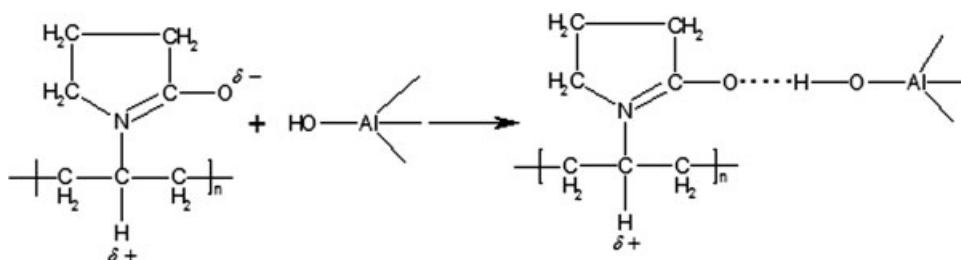


Figure 6 Schematic of the interaction between C=O group of the PVP and the surface —OH group of Al₂O₃ colloidal particles through a hydrogen bond.

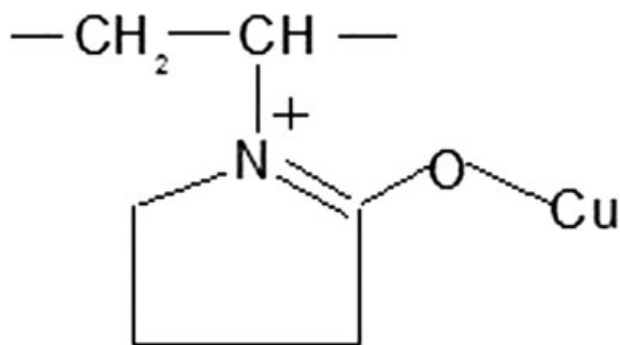


Figure 7 Schematic of the interaction between PVP and copper through oxygen.

etc.).^{35,38,41,42} A resultant complex with a basic structure of $\text{Fe}(\text{C}_6\text{H}_9\text{NO})_5$ has been demonstrated.³⁵ Schweinsberg et al. have confirmed that PVP interacts with copper through oxygen (see Fig. 7).⁴² Because of the interaction between PVP and metals, PVP has been used as inhibitors for the corrosion of Al, Fe, Cu, and low carbon steel.⁴¹ In this work, alumina sol was synthesized with PVP addition and was deposited on to steel substrate (containing Fe, Cr, and Ni atoms) to produce alumina/PVP hybrid film. So, this work involves the interactions between not only PVP and surface HO—Al groups of Al_2O_3 colloidal particles but also PVP and metal. The retard of the burning of PVP chains in the alumina/PVP hybrid gel implies the occurrence of interaction between PVP and Al_2O_3 particles. The improvement of adhesion of alumina film on metal with the addition of PVP confirms the occurrence of interaction between PVP and metal.

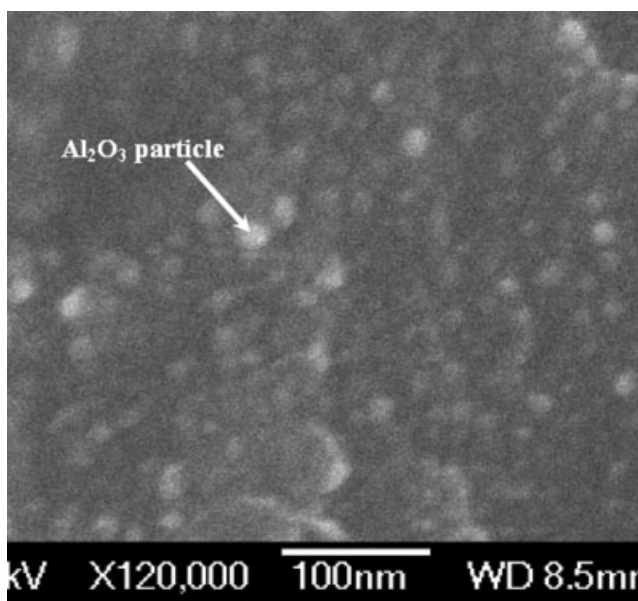


Figure 8 Cross-section morphology of a thick (1.5 mm) alumina/PVP hybrid film heated at 250°C for 30 min.

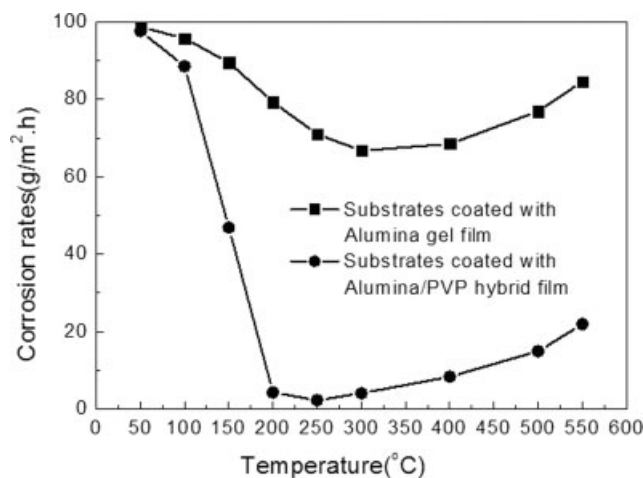


Figure 9 Corrosion rates of metallic substrate coated with alumina or alumina/PVP hybrid films plotted against heat treatment temperature.

It has been reported that PVP chains involves crosslink reaction when heat treated above 160°C.³⁵ In this work, whether the crosslink reaction takes place or not can be examined by investigating the solubility of PVP film sample in water. It is well known that the linear PVP molecules are quite dissolvable in water. If PVP molecules are not crosslinked, sooner or later the PVP film will dissolve in water. In this work, It was found that PVP film sample did not dissolve in water any more after heat treated above 160°C, confirming the occurrence of crosslink reaction. Because the crosslinked polymers show high strength it is believed the crosslink reaction is helpful to improve the antibreaking ability of the alumina/PVP samples. This was approved by the fact that the samples heat treated between 200 and 300°C show higher antibreaking abilities than those heat treated below 150°C. The coated samples that were heat treated between 300 and 600°C did not show very high antibreaking ability. This is because a heat treatment above 300°C would more or less damage the alumina/PVP hybrid structures. Therefore, alumina/PVP films with intact hybrid structures could be obtained by heat treatment between 200 and 300°C. Figure 8 gives the cross section morphology of a thick (1.5 mm) alumina/PVP gel film heat treated at 250°C for 30 min. The particles with a size of 20 nm were uniformly distributed in the material providing excellent interface interaction between alumina particles and PVP matrix. That is to say, nanoalumina particles reinforced PVP hybrid composite film was produced. Therefore, the antibreaking ability of the alumina/PVP hybrid film-coated metallic substrates was observed during adhesion test reaching the highest after heat treatment between 200 and 300°C.

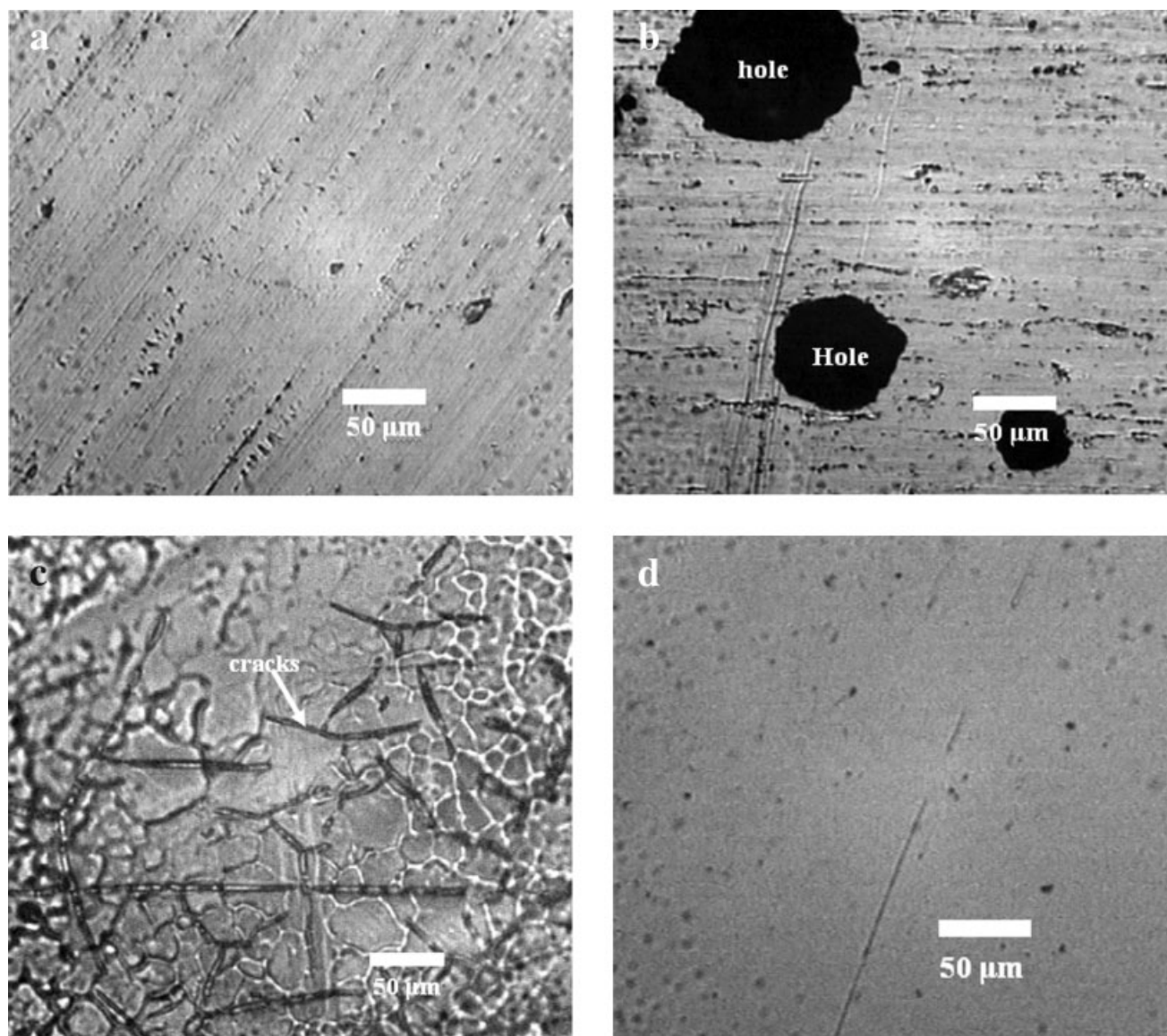


Figure 10 Optical micrographs of metallic substrates coated with no film (a,b), alumina film (c), and alumina/PVP hybrid film (d). The samples (b), (c), and (d) have been held in 6% ferric chloride solution at 35°C for 24 h. The samples (c) and (d) were heat treated at 250°C for 30 min before soaked in ferric chloride solution.

Corrosion resistance of coated metallic substrates

Figure 9 gives the changes in corrosion rates of coated metals with heat treatment temperature. The corrosion rates are calculated relative to the corrosion rate of the uncoated metallic substrate as 100%. The corrosion rate of uncoated metallic substrate was measured to be $9.95 \text{ g m}^{-2} \text{ h}^{-1}$. The specimens that were coated with alumina gel film and heat treated between 50 and 200°C exhibited comparable corrosion rates with that of the uncoated metal. It has been reported that the gelation of this alumina sol was reversible because the bonds responsible for gelation are weak bonding interaction of Van der Waals and hydrogen among the alumina colloidal particles.³³ For this reason, the coated alumina gel

film was found redissolving in the ferric chloride solution and providing no corrosion resistance. We have examined that the redissolving behavior of this alumina gel material could be sufficiently weakened after subjected to heat treatment at a temperature above 200°C. As a result, the corrosion rates of these samples that were heat treated above 200°C were observed decreasing, but due to the cracks, they still exhibited pretty high corrosion rates.

The samples that were coated with alumina/PVP hybrid films and heat treated below 100°C also showed comparable corrosion rates with that of the uncoated metal because the hybrid film was observed redissolving in the ferric chloride solution due to the reversible gelation of this alumina gel and the high dissolvability of linear PVP molecules in

water. The corrosion rates were decreased when the heat treatment temperature was increased up to 160°C because the linear PVP chains were cross-linked weakening the reversible gelation of this alumina gel material. Extra low corrosion rates (lower by 95% than uncoated metal) were obtained when the coated samples were heat treated between 200 and 300°C. Further increase of heat treatment temperature resulted in increase of corrosion rates because the alumina/PVP hybrid structures commenced subjecting to destruction by heat treatment at a temperature above 300°C. Therefore, the production of a coating film with perfect alumina/PVP hybrid structures is important to obtain excellent corrosion resistance for metal.

Figure 10(a) gives the optical image of the original metallic substrate. Figure 10(b) is the optical image taken after the original metallic substrate was held in 6% ferric chloride solution at 35°C for 24 h. Figure 10(c,d) are the optical images taken after the alumina or alumina/PVP hybrid film-coated metallic substrates were held in 6% ferric chloride solution at 35°C for 24 h. The samples shown in Figure 10(c,d) have been heat treated at 250°C for 30 min before served for corrosion resistance testing. The original metallic substrate had a pretty smooth surface, but an extreme coarse surface with big grooves and holes was produced after soaked in ferric chloride solution, manifesting the uncoated metal has been subjected to very serious corrosion. Similar morphology was observed in Figure 10(c), disclosing the alumina gel film without PVP could not effectively prevent the metal from corrosion. Figure 10(d) shows that no holes and grooves were observed after the sample was soaked in ferric chloride solution at 35°C for 24 h. The crimples observed in Figure 10(d) were produced during heat treatment at 250°C as a result of volume shrinkage. Actually, little change in the surface morphology was observed before and after this sample was soaked in ferric chloride solution. The alumina/PVP hybrid film was not observed to peel off after soaked in the ferric chloride solution for further 5 days. Therefore, the coating alumina/PVP hybrid film heated at 250°C could sufficiently protect the metal from corrosion.

CONCLUSIONS

Alumina sol with high oxide concentration, favorable viscosity, and low surface tension (lower by 34.7% than the sol without PVP) was synthesized with the addition of PVP. Compact, crack-free alumina/PVP hybrid film with a thickness up to 2 μm has been deposited onto metallic substrates by sol-gel dip-coating method. The hardness of the coated samples increased with the increment of heat treat-

ment temperature and a hardness value comparable with that of original metal was detected by heat treatment between 300 and 400°C. Alumina/PVP coating film with intact hybrid nanocomposite structures were produced on metal by heat treatment between 200 and 300°C, resulting in a good level of adhesion and extra low corrosion rates (lower by 95% than uncoated metal).

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