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FRACTAL POLYZIRCONOSILOXANE CLUSTER COATINGS

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ABSTRACT

Fractal polyzirconosiloxane (PZS) cluster films were prepared through the hydrolysis-polycondensation-pyrolysis synthesis of two-step HCl acid-NaOH base catalyzed sol precursors consisting of N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole, $\text{Zr}(\text{OC}_2\text{H}_5)_4$, methanol, and water. When amorphous PZSs were applied to aluminum as protective coatings against NaCl-induced corrosion, the effective film was that derived from the sol having a pH near the isoelectric point in the positive zeta potential region. The following four factors played an important role in assembling the protective PZS coating films: 1) a proper rate of condensation, 2) a moderate ratio of Si-O-Si to Si-O-Zr linkages formed in the PZS network, 3) hydrophobic characteristics, and 4) a specific microstructural geometry, in which large fractal clusters were linked together.

INTRODUCTION

We have described the characteristics of an inorganic polymetallosiloxane (PMS) film, formed by the pyrolysis of sol precursor-induced organopolymetallosiloxane xerogels, intended for use as corrosion-protective coatings on aluminum substrates^{1,2}. The chemical components of the precursor solution consisted of monomeric organosilanes, metal alkoxides [$\text{M}(\text{OC}_2\text{H}_5)_4$, M: Zr, Ti, and Ge], methanol, water, and hydrochloric acid. Our findings suggested that the following chemical factors play an important role in ensuring that the PMS coatings afford adequate protection : 1) the addition of HCl used as a hydrolysis accelerator for the organosilanes, and $\text{M}(\text{OC}_2\text{H}_5)_4$, which produces

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a clear sol solution, thereby aiding in the formation of smooth, uniform coating layers, 2) the organosilane to $M(OC_3H_7)_4$ ratios are critical in achieving spreadability of the sol solution on Al surfaces, and in leaving a minimum amount of organic and crystalline by-products in the organopolymetallosiloxane xerogel formed at a sintering temperature of $\approx 150^\circ C$, 3) moderate densifications of the Si-O-M linkages in amorphous PMS networks derived from the $300^\circ C$ -pyrolytic conversion of xerogel are needed to minimize the development of stress cracks in the films, and 4) the formation of covalent oxane bonds at the interfaces between the PMS and aluminum substrate increase the likelihood of strong adhesion forces.

However, all the present information on the PMS coatings were obtained from experiments with the sol precursor solution in the presence of acid catalysts. The objective of the present study was to investigate the characteristics of polyzirconosiloxane (PZS) coating films derived from two-step, acid-base-catalyzed precursors consisting of N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (TSPI), $Zr(OC_3H_7)_4$, methanol, and water, over a broad pH range of 1.0 to 13.0.

MATERIALS

N-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (TSPI), supplied by Petrarch Systems Ltd., and zirconium (IV)-isopropoxides [$Zr(OC_3H_7)_4$] obtained from Alfa Products, were used as the network-forming monomeric material. The film-forming mother-liquor, which served as the precursor solution, was prepared by incorporating the TSPI- $Zr(OC_3H_7)_4$ mixture into a methyl alcohol/water mixture containing HCl as a hydrolysis accelerator. HCl-catalyzed hydrolysis of the alkoxy groups in the TSPI and $Zr(OC_3H_7)_4$ provided a clear colloidal precursor solution. To increase the pH of the acid solution, NaOH as a condensation promoter was added to the mother-liquors. Table 1 shows the compositions of the precursor solutions prepared through such a two-step acid-base-catalyzed method, as a function of pH.

Table 1
Compositions of Sol Precursor Solutions in The pH Range of 1.1 to 12.8

pH	TSPI wt%	$Zr(OC_3H_7)_4$ wt%	CH ₃ OH wt%	Water wt%	HCl wt% / TSPI + $Zr(OC_3H_7)_4$	NaOH wt% / TSPI + $Zr(OC_3H_7)_4$
1.1	7.7	5.1	7.7	79.5	50.0	0.0
2.6	7.7	5.1	7.7	79.5	50.0	10.4
7.1	7.7	5.1	7.7	79.5	50.0	14.0
8.6	7.7	5.1	7.7	79.5	50.0	18.0
11.5	7.7	5.1	7.7	79.5	50.0	26.0
12.8	7.7	5.1	7.7	79.5	50.0	39.0

The metal substrate was 6061-T6 aluminum sheet, containing the following chemical constituents: 96.3 wt% Al, 0.6 wt% Si, 0.7 wt% Fe, 0.3 wt% Cu, 0.2 wt% Mn, 1.0 wt% Mg, 0.2 wt% Cr, 0.3 wt% Zn, 0.2 wt% Ti, and 0.2 wt% other.

The aluminum surfaces were coated by PZS xerogels in the following sequence. The aluminum surfaces were wiped with acetone-soaked tissues to remove any gross surface contaminants. The aluminum substrates were then dipped into the colloidal precursor solution at ambient temperature. After dipping, the substrates were withdrawn slowly from the soaking bath. The precursor-wetted substrate surfaces were preheated in an oven for 30 min at 100°C to yield a xerogel coating film. The xerogel films were subsequently pyrolyzed for 15 min in air at temperatures of 250°-300°C.

RESULTS AND DISCUSSION

SOL PRECURSOR SOLUTIONS

Because a sol is a colloidal suspension of solid particles in a liquid, the zeta potential (z-p), is an important guide to understanding the growth rate of colloidal and polymeric solid particles. Figure 1 shows the variation of z-p value as a function of the pH of the precursor solution. The particle size of these clusters in an aqueous solution may range from ≈ 1 to ≈ 20 nm³.

Figure 1. Changes in zeta potential as a function of the pH of the sol precursors.

At pH 1.1, the protons, H^+ , in the solution favorably attack the negative hydroxyl groups on the cluster particles; consequently, the overall net effective charge on the polydispersities measures + 26.7 mV. When NaOH was incorporated into this acid precursor solution, the presence of OH^- led to a charge reversal. As shown in the resultant curve, the z-p value decreases progressively with the increased pH of the solutions. The isoelectric point (IEP), where there is no net charge (zero mV of z-p) on the particle surfaces, occurs around pH 9.5. With further increase in pH, the z-p charge becomes negative; beyond a pH of 11.5, the surface charge shifts to near zero potential in the negative regions.

To better understand these data, the microstructure of xerogel films deposited on the aluminum (Al) substrate was observed with SEM. The films were prepared in a vacuum oven at 70°C. The surface images of films from sols with pH 1.1, 2.6, 8.6, and 11.5, are shown in Figures 2 and 3. The SEM micrograph (fig. 2-a) of the pH 1.1 sol-derived xerogel display the continuous features of a smooth transparent film. As seen in Figure 2-(b), an increase in the pH from 1.1 to 2.6 resulted in a change in the morphology of film, which then showed two different cluster species, a randomly distributed branch-type polymer, and a transparent-type polymer. With a sol of pH 8.6, which is near the IEP, the microtexture of film (fig. 3-c) disclosed a compacted version of highly branched clusters, which completely covered the Al substrates. There were no transparent-type clusters present. Thus, use of the combination of acid and base catalysts promotes decoupling between hydrolysis and condensation. At pH 11.5, the SEM image (fig. 3-d) showed that the film had a large number of microcracks. The reason for the development of microcracks may be due to the chemical reaction between high pH precursor and Al substrate; namely, the OH^- ions in the precursor favorably react with Al ion in the Al oxides lattice to promote the pitting-type corrosion of Al alloys^{4,5}. Such an interfacial reaction may lead to bond breakage and reformation of the primary building polymer conformation.

Before surveying the properties of the pyrolyzed PZS films deposited on the Al substrates, we investigated the thermal behavior of Zr-incorporated organosilanes derived from sols with different pHs, using TGA-DTA. Figure 4 illustrates the TGA and DTA curves which reveal the decomposition characteristics during pyrolysis of samples of 150°C-preheated xerogel powders. The TGA curve for the sol-derived xerogel samples at pH 1.1 indicates that there are three decomposition states; the first begins at the onset temperature (T_{d1}) near 250°C, the second occurs between $\approx 380^\circ$ and $\approx 470^\circ C$, and the third from $\approx 500^\circ$ to $\approx 610^\circ C$.

Figure 2. SEM micrographs for Ph (a) 1.1 sol- and (b) 2.6 sol- derived xerogel films deposited on the aluminum surfaces.

Figure 3. SEM images for pH (c) 8.6 sol- and (d) 11.5 sol-derived xerogel films deposited on aluminum surfaces.

Compared to the TGA curve of the pH 1.1 samples, the shape of the curve changes in the NaOH-incorporated samples. There are three notable differences: 1) an increase in the pH of the sol lowers the temperature of onset of thermal decomposition in the third stage, 2) the intensity of the DTA peak at 420°C, corresponding to the second decomposition, significantly decreases, and 3) the total weight loss of samples at 610°C decreases with increasing pH. These findings imply that NaOH-catalyzed condensation plays an important role in forming the xerogel containing a low concentration of removable carbonaceous groups and moisture, and in promoting the conversion of the organic-inorganic mixed phase into the inorganic phase at a relatively low temperature.

XEROGEL COATING FILMS

On the basis of this information, xerogel films were deposited on the Al substrate surfaces by a dipping method. The thickness of 100°C-dried films, measured with a surface profile system, ranged from 0.6 to 1.2 μm . The pyrolytic changes and rearrangement in conformation of 100°C-sintered film samples at 300°C were investigated with specular reflectance IR.

Figure 5 shows the changes in the IR spectral features of 300°C-pyrolyzed xerogel films. The changes in the spectral structure of the pH 1.1 film (a), compared with that of a 150°C-preheated sample (not shown), can be described as follows: 1) the elimination of the peaks at frequencies at 1300 and 1190 cm^{-1}

Figure 4. TGA and DTA curves for the pyrolysis of xerogels heated in air at a rate of 10°C/min.

originating from the Zr-O-C and Si-C bands, respectively, 2) a shift in the absorption of the Si-O-C band, while its peak intensity becomes much weaker, and 3) a shift in the Si-O-Zr band from 930 to 970 cm^{-1} . The first two results are indicative of the removal of many carbonaceous groups from the polymeric organozirconosiloxane networks. Such pyrolytic phenomena will lead to the third result, namely, the PZS network structure at 300°C has a high degree of densification of Si-O-Zr linkages. For all of the NaOH catalyst-induced films, the peak absorbance of the Si-O-Zr band at 970 cm^{-1} grows conspicuously with the increase in concentration of NaOH, suggesting that the extent of densification of Si-O-Zr linkage in the formed PZS films is related strongly to the pH of sol. On the other hand, the signal intensity of Si-O-Si band at 1010 cm^{-1} declines with a rise in pH.

The EDX spectrum (not shown) of the 300°C-pyrolyzed pH 1.1 film, in the absence of an NaOH catalyst, has three prominent lines, corresponding to Si, Zr, and Cl elements. The Si and Zr elements virtually belong to the PZS, while the presence of Cl is associated with the HCl used as hydrolysis promoter of the alkoxy groups in the TSPI and $\text{Zr}(\text{OC}_3\text{H}_7)_4$. When the pH of this HCl catalyst-induced sol was adjusted to 2.6 by adding NaOH, the EDX spectral structure is characterized by a remarkable increase in the signal intensity of Cl, and a signal of Na emerges. A further increase in NaOH in the sol system results in the specific features of spectrum, involving a significantly intensified Cl signal and a growing intensification of the Na line. Thus, the acceleration of the rate of the condensation reaction by the NaOH catalyst not only contributes to an increase in densification of Si-O-Zr linkages, but also promotes the formation of Na-related Cl compounds as by-products in the PZS layers.

To further demonstrate that the NaCl by-product had been removed from the PZS layers, we inspected the depth-elemental composition profile in the water-rinsed pH 8.6 film layers and in the PZS/Al interfacial regions, using auger electron spectroscopy (AES) in conjunction with Ar ion sputter-etching. The sputter rate for the depth profiling was $\approx 30 \text{ nm/min}$. Figure 6 depicts the changes in auger peak heights of representative elements such as O, Si, Zr, Cl, and Al versus sputter time for the pH 8.6 film deposited on Al samples. The Cl at the surface of the film (zero sputter time) had the lowest peak, corresponding to a minor atomic presence. The height of the peak decreased with sputter times and then disappeared at a depth of $\approx 540 \text{ nm}$. This finding implies that there is no Cl in the PZS layers adjacent to the Al substrate.

In making water-impermeable xerogel films, the magnitude of wettability of the coating's surfaces by water is among the most important factors governing good protective performance. Therefore, the degree of the water-wettability of the xerogel

Figure 5. IR spectra for the 300°C-pyrolyzed xerogels at ph (a) 1.1 (b) 2.6, (c) 8.6, (d) 11.5, and (e) 12.8.

Figure 6. AES depth-profile of pyrolyzed PZS-coated aluminum after rinsing with water.

film surface was estimated from the average value of the advancing contact angle on this surface. Figure 7 is a plot of θ (degree) as a function of the film-treating temperatures, for the pH 8.6 film. Since a high contact angle correlates with a low rate of wetting, the resultant θ -temperature curve showed that film surfaces treated with a high temperature are less wettable. As the film is exposed to high temperatures the original hydrophilic xerogel surfaces are converted to hydrophobic surfaces. The θ value similar to that of the 250°C film was obtained from the 300°C-treated film, suggesting that PZS films having a minimum water-wetting behavior can be prepared by pyrolysis at temperatures of $\geq 250^\circ\text{C}$.

Figure 8 illustrates the variation in I_{corr} value of Al substrate as a function of the treating temperatures for pH 1.1, 2.6, 7.1, 8.6, and 12.8 sol-derived PZS coating films. The protective ability of the coatings depends primarily on the pH value of sol precursors and the treatment temperature of films. The I_{corr} value for the coatings preheated at 100°C ranged from 0.2 to 1.9 μA . Since a low I_{corr} value is predictive of good corrosion protection, such a high I_{corr} represents poor protection. The major reason for the poor protection is due to the hydrophilic nature of coatings, which have a high susceptibility to water-wettability. In fact, all the films were dissolved after immersion for ≈ 10 hr in a water at 25°C. A reduction in I_{corr} to a low current density was measured for all films treated at 200°C, except for the pH 12.8 coating. Increasing the temperature of treatment to 250°C acted to further reduce the I_{corr} ; beyond this temperature, there was only a slight decrease in I_{corr} . Therefore, films treated at temperatures $\geq 250^\circ\text{C}$ have the maximum ability to protect Al substrates. In contrast, the I_{corr} of 200°C-treated pH 1.1 film tends to increase with increased temperature. This phenomenon can be associated with failure of the film, induced by high shrinkage that is related to the liberation of many carbonaceous groups at elevated temperatures, thereby resulting in a poor protection performance. The ability of 300°C-treated films to protect Al was rated in the following order: pH 8.6 > 7.1 > 2.6 > 12.8 > 1.1. This finding strongly suggested that a dense PZS fractal cluster coating containing a proper proportion of Si-O-Si to Si-O-Zr linkages provides an effective barrier to the corrosion of Al substrate and minimizes the corrosion rates of Al.

Figure 7. Effect of temperature on the reduction of water-wettability of xerogel film surfaces.

Figure 8. Changes in the corrosion current, I_{corr} , of PZS xerogel-coated aluminum substrates as a function of temperatures of treatment of the coatings; pH 1.1 (o), 2.6 (Δ), 7.1 ($\square$), 8.6 ($\bullet$), and 12.8 (x).

CONCLUSIONS

An increase in the pH of the sol (by adding an appropriate amount of NaOH), reflecting the progression of the condensation reaction, led to a significant growth of cluster particles. This cluster growth significantly contributed to a shift in the zeta potential (z-p) of the sol to near zero mV in the positive potential regions. The morphology of this sol particle was characterized by fractal cluster species having highly branched microfeatures. These clusters eventually link together to build ideal xerogel films with particle-packing geometries. The isoelectric point (IEP) of the sol, corresponding to the 0 mV of z-p, seems to occur around pH 9.5. The molecular structure of xerogel made from the sol with near IEP at the positive potential sites exhibited a moderate densification of Si-O-Zr linkages, reflecting the deposition of ideal fractal cluster films on the aluminum substrates.

The hydrophobic PZS fractal cluster coating, which is most reliable in protecting the aluminum substrate against NaCl-induced corrosion, can be prepared by the pyrolysis at 250°-300°C, of the xerogel film from sol at pH 8.6.

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