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ELECTROCHEMICAL PROPERTIES OF MELTING GEL COATINGS

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ABSTRACT

Organic-inorganic melting gel coatings were applied to titanium alloy substrates to decrease their corrosion and extend their lifetime in an electrochemical application. Melting gels containing phenyl substitutions were coated onto the substrates. The ratio of diphenyl dimethoxysilane (DPhDMS) to methanol was varied to change the thickness of the coatings. The coatings were inspected visually to see that there is good adhesion between the coating and the substrate. Nanoindenter tests were performed to determine hardness.

INTRODUCTION

Organic-inorganic hybrid sol-gel coatings have been formulated to protect a variety of metals¹. In particular, stainless steel has been a common subject of these coating studies because it is used in a variety of electrochemical systems, often as the current collector in fuel cells^{2,3}. The emphasis of many studies of metal corrosion is to reduce the need for chromate-based chemical conversion coatings^{4,5,6}. The protection mechanism of the coatings are one or more of the following: barrier properties, cathodic protection, and inhibition and passivation. The primary function of the melting gel coatings in this investigation is a barrier layer^{7,8}.

In a previous study using melting gels as barrier materials⁷, lithium metal was mounted on mica and sealed with melting gel. After consolidation, a melting gel with molar ratio 1.0 mole PhTMS (phenyltrimethoxysilane)-0.15 mole DPhDMS (diphenyl dimethoxysilane) was monitored for degradation of the lithium metal. This was determined visually. Initially, the lithium metal was shiny, but gas transport through the gel caused the surface of the metal to change due to the formation of Li₃N. Using an areal calculation, a degradation constant was estimated ($K_{diff} = 0.00192 (\%) \text{ sec}^{-1/2}$), which allowed the estimate of a total time to decay of greater than 68 years. The benefits of melting gel coatings depend on their hydrophobic character, their absence of porosity, and their adhesion^{9,10,11}. Also, the melting gels are applied at low temperature, which precludes oxidation of the metal substrate during the application¹².

Previous efforts to treat metal surfaces with sol-gel materials include mineralization treatments with sodium silicates⁴. These coatings are effective on galvanized steel. Other treatments have been applied in a spray operation with mixtures of tetraethylorthosilicate (TEOS) and methyltriethoxysilane (MTES) on 304 stainless steel⁵ or dipped⁶. The sprayed layers were followed by dip coatings to decrease the surface roughness. In addition to the organically modified sol-gel coatings, some coatings have been prepared with TEOS, 3-methacryloxy propyl trimethoxysilane (MPTS) followed by thermal curing with methyl methacrylate on mild steel¹³.

Besides the studies on steels, there are studies of organic-inorganic coatings for aluminum alloys. For example, TEOS and triethoxy octylsilane (TEOCS) has been tested on aluminum alloys such as AA2024¹⁴. Another study reported coatings based on TEOS and 3-glycidioxypropyl trimethoxysilane (GPTS), combined with cerium phosphate inhibitors¹⁵. Organic-inorganic coatings have been prepared with TEOS and 3-methoxy silylpropyl methacrylate (TSPM) with TiO_2 - CeO_2 nanoparticles as inhibitors¹⁶ and with SiO_2 nanoparticles for reinforcement¹⁷. These coatings were applied to AA2024 and tested in a 3.5% NaCl solution. In addition, there are organic-inorganic hybrids developed especially for copper that incorporate clay particles in phenyl trimethoxysilane (PhTMS)¹⁸. A final example used GPTS and incorporated microcontainers with poly(ethylene imine) and poly(styrene sulfonate), which could be released to enable self-healing¹⁹.

Recently, a study was carried out with melting gels in the methyl-substituted family, using methyltriethoxysilane (MTES) and dimethyldiethoxysilane (DMEDES)². Thick (> 0.5 mm) hybrid glass coatings were obtained by consolidation of methyl substituted melting gels on AISI 304 Stainless Steel. The presence of methyl moieties and a Si-O-Si backbone were confirmed by FT-IR and Raman spectra. Both SEM analysis of the cross-section and micro-scratch tests showed homogeneous, thick, crack-free and well-bonded coatings with largely plastic deformation behavior. Electrochemical characterization (potentiodynamic polarization and electrochemical impedance spectroscopy) in NaCl 3.5% wt. solution indicated very stable surface films that showed no breakdown after four months of immersion. Current densities in polarization curves were as low as 10^{-3} nA/cm², six orders of magnitude lower in comparison to the bare substrate. Impedance measurements also presented an excellent behavior with values around 10^{11} ohms, six orders of magnitude higher than the bare substrate.

In this study, a formulation similar to the one tested with lithium metal has been used. Because the melting gel in this case is applied directly to metal substrates, a systematic variation of the solvent to water ratio was investigated. That is the water to PhTMS ratio was held constant, and the amount of methanol used to dilute the DPhDMS component was varied. A previous composition was duplicated¹¹, and then the amount of methanol was doubled and doubled again. The reason for increasing the methanol was to control the viscosity of the solution. Previous studies changed the viscosity by changing the precursor, using phenyl and methyl substitutions, and changing the reactive groups from methoxy to ethoxy. Based on these previous studies, it was expected that the methanol acts to dilute, which can delay cross-linking or facilitate condensation²⁰. Moreover, the higher amount of solvent allows longer time of reaction and a better formation of the inorganic network. In this way, it is possible to adjust the glass transition temperature. In addition, the methanol content may help to control the thickness of coating in dipping or pouring, and its careful removal can help prevent cracking during drying and cooling from the consolidation temperature.

EXPERIMENTAL PROCEDURE

Synthesis

The preparation of the melting gel was carried out using a pair of mono- and disubstituted alkoxysilanes, PhTMS (Gelest Inc., Morrisville, PA) with DPhDMS (Gelest Inc.). All of the substituted alkoxysilanes were used without further purification. Hydrochloric acid (Fisher Scientific, Atlanta, GA) was used as a catalyst. As a solvent, anhydrous methanol (Sigma-Aldrich, Milwaukee, WI) was used with PhMTMS-DPhDMS. These gels were prepared using 1 mole of mono- to 0.25 moles of di-substituted alkoxysilane. A two-step synthesis was used. First, the PhTMS and water were mixed together. The molar ratio of PhTMS:H₂O was 1:1.5. The pH of the water was adjusted to 2.5 using a 0.1 M HCl solution.

After the water was added to the PhTMS, the mixture was stirred continuously at 40°C in a covered beaker. In the absence of a cosolvent, the mixture initially showed immiscibility between water and PhTMS. A clear solution was obtained after 30 min of stirring, and stirring was continued for 6 hours.

In the second step, DPhDMS was diluted with methanol. The molar ratio was 4, 8 or 16 moles alcohol to 1 mole DPhDMS. The DPhDMS-methanol mixture was added dropwise to the clear solution of PhTMS and water. This mixture was stirred for another two hours in a closed beaker at 40°C. Then, the clear solution was cooled to room temperature and stirred overnight in an open system until it gelled. The gels were then dried at 70°C for 24 h, followed by a heat treatment at 110°C. After this heat treatment, the gels were rigid at room temperature, but they resoftened at ~100°C.

Sample Coating

The titanium alloy substrate was prepared by gently rubbing with SiC abrasive paper (P2400/6.5 μm), followed by cleaning in isopropanol in an ultrasonic bath. The previously prepared melting gel was softened at 100°C. Approximately the same amount of gel was poured each time onto the substrate. The coated samples were placed in an oven and heated to 150°C for 24, 48 or 96 hours before cooling back to room temperature, which took about 4 hours. A typical sample is shown in Figure 1.

Figure 1. Comparison of the coated side (a) and the uncoated side (b) and stored in ambient conditions for 6 months

Nanoindentation

A Hysitron Triboindenter (Minneapolis, MN) was used with a Berkovich tip with a roughly 100 nm tip radius. As a nanoindenter, it is instrumented allowing for continuous measurement of both depth and load. In operation, the pyramidal tip is gently pushed into the sample, and load and depth are recorded. During unloading, the modulus and hardness are calculated. The instrument is calibrated using a fused quartz standard. The loading conditions were 1 mN and 3 mN, and a loading cycle of 10 s load and 10 s unload. For each indentation load, three indents were made, averaged and the standard deviation was calculated.

RESULTS

The composition with 4 moles of methanol was duplicated from an earlier study ($T_g = 21^\circ\text{C}$)¹¹. The consolidation temperature, after which the gels no longer soften, was determined experimentally. The consolidation temperature for this melting gel is 180°C , as previously determined for gels with 4 moles methanol. That value was determined in a bulk sample. In the case of the coatings on titanium alloy, the consolidation occurred by heating for 1 day at 150 or 200°C , followed by a slow cool of about 4 hrs. The results of the indentation hardness measurements are shown in Table 1.

Table 1. Hardness measurements on melting gels after consolidation

	Mole Ratio						
PhTMS	DPhDMS	Methanol	Heat Treatment	Time	Hardness 1mN	Hardness 3mN	Cracked
			$^\circ\text{C}$	hours	MPa	MPa	
1	0.25	4	150	48	169 ± 1.2	170 ± 0.9	No
1	0.25	8	150	48	211 ± 5.8	220 ± 3.0	Yes
1	0.25	16	150	48	113 ± 0.8	121 ± 0.8	No
1	0.25	4	150	96	-	192 ± 5.3	No
1	0.25	8	150	96	207 ± 3.6	211 ± 1.8	Yes
1	0.25	16	150	96	164 ± 0.2	169 ± 4.6	No
1	0.25	4	200	24	165 ± 4.3	150 ± 17.7	Yes
1	0.25	8	200	24	214 ± 8.8	221 ± 5.4	Yes
1	0.25	16	200	24	144 ± 2.8	-	Yes

A total of 9 samples are listed in Table 1. The molar ratio of PhTMS to DPhDMS is the same in all cases. The level of methanol is increased from 4 to 8 to 16. The heat treatment temperature is either 150 or 200°C . For the samples at 150°C , the difference is the time of treatment, either 48 hr or 96 hr. All of the samples at 200°C cracked.

Indentation curves for loading and unloading are shown in Figure 2. The samples in this case were heated for 96 hr at 150°C , and the curves were recorded for 1 mN load. The 3 curves for the samples with 8 and 16 moles of methanol are almost indistinguishable. There is considerable variation in the sample with 4 moles, reflecting a nonuniform surface. Each sample was tested at 1 mN and 3 mN (not shown). The hardness appears to be independent of load.

Figure 2. Indentation hardness for 96 hours at 150°C and 1 mN load for 4:1, 8:1 and 16:1 moles methanol to DPhDMS

Doubling the time from 48 hr to 96 hr at 150°C increased the hardness somewhat. Doubling the methanol made the gel more fluid for pouring, but harder when consolidated. The samples with 8 moles of methanol cracked. Increasing methanol to 16 moles introduced surface "stickiness", but these samples were less likely to crack than at 8 moles.

The best crack-free coatings were formed using a treatment of 1 day at 150°, followed by 6 days at 110°C and a 4 hour furnace cool to room temperature. To see the benefits of the coating, compare the samples side by side in Figure 1. The coated side of the sample (a) is still shiny, while the uncoated side of the sample (b) is showing serious corrosion damage after 6 months.

SUMMARY

As seen previously, melting gels provide a barrier mechanism for corrosion protection. The surface is hydrophobic. The layer is nonporous. Diffusion through the layer is limiting. Further electrochemical testing is being carried out at CSIC. To further improve the protection provided by the melting gels addition of inhibitors (e.g., Ce) is being planned.

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