1. Introduction to Sol-Gel

A sol is a dispersion of the solid particles (~ 0.1-1 μm) in a liquid where only the Brownian motions suspend the particles. A gel is a state where both liquid and solid are dispersed in each other, which presents a solid network containing liquid components. The sol-gel coating process usually consists of 4 steps:

(1) The desired colloidal particles once dispersed in a liquid to form a sol.

(2) The deposition of sol solution produces the coatings on the substrates by spraying, dipping or spinning.

(3) The particles in sol are polymerized through the removal of the stabilizing components and produce a gel in a state of a continuous network.

(4) The final heat treatments pyrolyze the remaining organic or inorganic components and form an amorphous or crystalline coating[1-4]

There are two distinct reactions in the sol-gel process: hydrolysis of the alcohol groups and condensation of the resulting hydroxyl groups. In the case of isomorphous γ-AlOOH precursor, it exists as the un-hydrolyzed species [Al(OH2)6]3+ below pH 3 [1], and can be hydrolyzed extensively with increasing pH:

\[
[Al(OH_2)_6]^{2+} + kH_2O \rightarrow [Al(OH)_k(OH_2)_{6-k}]^{(2-k)+} + kH_2O^+ \quad (1)
\]

\[
hH_3O^+ + kOH^- \rightarrow 2kH_2O \quad (2)
\]

where \( h \) is defined as the molar ratio of hydrolysis.[2]

People generally agree that the preferred condensation sites are those that maximize the interactions between lone pair electrons on a bound hydroxide ligand on one aluminium species with a proton on a water-molecule bound to another aluminium species.[1] For example, two singly-hydrolyzed monomers (\( h=1 \)) condense to a dimmer via an olation reaction:

\[
2[Al(H_2O)_6^{2+} - H^+ \rightarrow Al(H_2O)_5OH^{2+}] - 2H_2O \rightarrow Al_2(OH)_3(H_2O)_8^{4+} \quad [1] \quad (3)
\]

However, the condensation mechanism of aluminium isopropoxide is more complex than the above description. People do not have very well understanding of the hydrolysis of the aluminium alkoxides.

2. Advantages of Sol-Gel Technique

* Can produce thin bond-coating to provide excellent adhesion between the metallic substrate and the top
* Can produce thick coating to provide corrosion protection performance.

* Can easily shape materials into complex geometries in a gel state.

* Can produce high purity products because the organo-metallic precursor of the desired ceramic oxides can be mixed, dissolved in a specified solvent and hydrolyzed into a sol, and subsequently a gel, the composition can be highly controllable.

* Can have low temperature sintering capability, usually 200-600°C.

* Can provide a simple, economic and effective method to produce high quality coatings.

3. Previous Limitations of Sol-Gel Technique

Despite its advantages, sol-gel technique never arrives at its full industrial potential due to some limitations, e.g. weak bonding, low wear-resistance, high permeability, and difficult controlling of porosity. In particular the limit of the maximum coating thickness is 0.5 μm when the crack-free property is an indispensable requirement[4]. The trapped organics with the thick coating often result in failure during thermal process. The present sol-gel technique is very substrate-dependent, and the thermal expansion mismatch limits the wide application of sol-gel technique.

4. Advantages of Polymer Components in Sol-Gel Ceramic Coatings

Some substrates, such as mild steel are prone to corrosion during aqueous CB-CSG processing, which typically proceeds in acidic environment of pH=2-4. A conventional method to address this matter is to phosphate the substrate, e.g. using zinc or iron phosphate[9]. However, these thin (less than a few microns) and micro-porous phosphate films are unstable at the elevated process temperature of chemical bonding of 300°C that may lead to additional interfacial porosity and opening again access of corrosive species to steel surface. Such coating system will not provide long-term corrosion protection to the steel surface.

![Fig.1: Comparison of conventional and new sol-gel coating on mild steel (MS)](http://www.ceramics.mmat.ubc.ca/introduction.html)
In order to overcome some of the limitations of traditional CB-CSG coatings, we have developed a non-porous and thermally stable “bond-coat” alumina reinforced siloxane film (ASMC) on a mild steel surface (Fig. 1.1), which would protect the surface both during CB-CSG processing, as well as provide a non-permeable membrane for corrosion protection in storage and service. Therefore, in this system the "topcoat" of CB-CSG protects the siloxane bond coat (and the metallic substrate) from the wear damage. The siloxane bond coat provides a fluid impermeable function and relieves the thermal stresses. We sometimes term it "multi-layer functionally graded bond coating" (FGBC).

At the initial stage, we hypothesized that the multilayer functionally gradient coating systems additionally benefited from relaxing interfacial thermal-strain during cooling from the process temperature through elastic and plastic deformation of the siloxane bond coat, which notably increased the bond strength of the entire coating system by releasing the energy of the CTE mismatch. Moreover, we will note that this bond strength increased the intrinsic adhesion of the coating significantly by its unique way of relaxing the thermal stress.

However, if polymeric components were directly added into the ceramic sol, people usually think that it will risk reducing the connectivity of the sol-gel network and decreasing condensation reaction rates (i.e., a longer time) during the gelling which, in turn, will result in a less dense microstructure of gel network upon the removal of solvent. If the impregnation of polymer took place after the gel process, it is believed that it will prevent the reduced adhesion between the coating and substrate, and then decrease the permeability. This is why we tried to use the polymer to post-treat the coating.

References:


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