Chapter 8
Sol-gel deposited silica coatings on different metal substrates

8.1 Introduction

Metals have great demand in the chemical and microelectronics industries due to their high thermal and electrical conductivities. A notable disadvantage in the use of metals is that they easily get corroded in aqueous atmospheres. Corrosion control is an important subject of increasing interest to the modern metal finishing industry. The development of coatings that provide the necessary protection of the metal surface is essential for its efficient use in these applications [1]. Surface modification of metallic substrates by organic or polymeric coatings is an essential approach for enhancing surface properties such as wear, oxidation, and corrosion. Various conventional techniques are utilized to depositing the desired materials onto the metallic substrate to achieve surface modifications with better protection for the substrate. Corrosion is a natural process that has troubled human beings ever since the use of metals. Hence, efforts to develop more efficient and environmentally compliant methods to prevent corrosion have been ongoing throughout this century [2]. In the past few decades, a great number of synthetic methods have been developed to fabricate non-metallic surfaces with special wettability. The construction of special wettability on metallic substrates is a scientifically and technologically challenging target. Recently, in order to extend the applications of metals, a variety of metallic surfaces with special wettability has been constructed by using different synthetic processes [3]. These metallic surfaces with special wettability exhibit some important applications such as anti-corrosion, oil–water separation, friction reduction, liquid transportation, and microfluidic materials.

Until now, different approaches have been described in the literature for the fabrication of superhydrophobic metal surfaces. The use of conducting polymers as advanced coating materials for corrosion protection of oxidizable metals has become one of the most exciting new research fields in recent times [4–9]. Qu et al. have reported a novel mixed-solution system for the fabrication of the superhydrophobic surface on steel, copper alloy and titanium alloy by a chemical etching method [10]. Wang et al. have fabricated a stable bionic superhydrophobic surface by immersing a copper plate into a solution of fatty acid [11]. The sol–gel coating on metals is relatively recent and has not been sufficiently investigated, in spite of its potential technological
interest. The basic concept of chemical conversion of metal surfaces is based on the deposition of a hydrophobic sol–gel barrier layer for surface protection and corrosion prevention [12].

Sol–gel-derived coatings have been found to be useful for a number of applications mainly due to the simplicity of solution based processing and the synthesis flexibility, which can be used for forming a wide range of thin films and coatings by using dip, spin or spray methods [13]. In addition, the use of organically modified precursors provides unique opportunities to tailor the physical and chemical properties of the final materials. Due to the presence of an organic component, the organosilica coatings dry evenly and are uniform and crack-free as compared to pure silica coatings. While there has been significant research activity in the use of sol–gel coatings for corrosion protection [14–16]. In the present study we reported, the methytrimethoxysilane based superhydrophobic silica coatings on different metal substrates for anticorrosion purpose with the simple dip coating method. The aim of this study is to test the capability of sol–gel coatings to improve corrosion resistance of the different metal substrates. It is found that the coatings are effective at preventing corrosion of copper, aluminium and brass substrates. In addition, the reproducibility is very good and we can get the similar result in every experiment under the preparation conditions. Overall, the strategy presented herein may provide a generic approach for fabrication of protective coatings on different metallic surfaces.

8.2 Experimental

8.2.1 Materials

The chemicals used were methyltrimethoxysilane, (Sigma–Aldrich Chemie, Germany), methanol (Loba Chem Limited, Mumbai), and ammonia (NH3, sp.gr.0.91, Qualigens Fine Chemicals, Mumbai). Poly-methylmethacrylate (PMMA). Double distilled water was used for all the experiments. All the reagents were used as received. Different metal substrates such as, copper, aluminium and brass are taken for the deposition.

8.2.2 Preparation of coating surfaces

The aluminum, brass and copper substrates were cleaned in order to get uniform deposition. Pieces of 1 cm × 5 cm were cut from above mentioned metal sheets and those are used as substrates. These substrates were mechanically polished using zero grade polish paper as an abrasive. This practice removed the grease and the native oxide layer from the surface of the metal plates.
8.2.3 Synthesis of superhydrophobic coatings

In the present investigation, our approach is to develop transparent antici-
corrosive superhydrophobic coatings on a various metal substrates through single step sol-gel based coating by using simple dip coating method. Such coatings consist of a low energy material and dual scale surface roughness in a hierarchical manner. The superhydrophobic silica coatings synthesized using the procedure described as bellow.

The methyltrimethoxysilane (MTMS) based organically modified alcosol is used for the deposition on a different metal substrates. A coating sol was prepared by keeping the molar ratio of MTMS: MeOH: H₂O constant at 1: 5.63: 1.58, respectively with PMMA (7 wt%) and (0.5 M) NH₄F as a catalyst for which we get maximum hydrophobicity. The cleaned metal substrates were dipped vertically after addition of base catalyst in the sol and taken out prior to gelation. Further, these substrates were annealed at 150 °C for 3 h to remove residual solvent.

8.3 Results and discussion

8.3.1 Reaction mechanism

The hydrolysis and condensation of methanol diluted MTMS in the presence of PMMA and NH₄F are as shown in following chemical reactions [17],

\[
\text{CH}_3\text{Si(OCH}_3\text{)}_3 + 3\text{H}_2\text{O} \xrightarrow{\text{NH}_4\text{F}} \text{CH}_3\text{–Si(OH)}_3 + 3\text{CH}_3\text{OH} \quad (8.1)
\]

\[
\begin{align*}
\text{CH}_3\text{–Si–OH} + \text{OH–Si–CH}_3 &\rightarrow \text{CH}_3\text{–Si–O–Si–CH}_3 + \text{H}_2\text{O} \\
\text{OH} &\quad \text{OH} &\quad \text{OH} &\quad \text{OH} \\
\text{OH} &\quad \text{OH} &\quad \text{OH} &\quad \text{OH}
\end{align*} \quad (8.2)
\]

\[
\begin{align*}
\text{CH}_3\text{–Si–O–Si–CH}_3 + \text{H}_3\text{CO–Si–OCH}_3 &\rightarrow \text{OH–Si–O–Si–O–Si–OCH}_3 + \text{CH}_3\text{OH} \\
\text{OH} &\quad \text{OH} &\quad \text{OCH}_3 &\quad \text{OH} &\quad \text{OH} &\quad \text{OCH}_3
\end{align*} \quad (8.3)
\]
The expected polymerization reaction between the hydrolyzed MTMS and PMMA is as shown in the reaction (8.4). The surface –OH groups are replaced by the CH₃ groups of the PMMA in order to achieve the inherent superhydrophobicity as well as nanostructured silica network resulted on the substrate surface with release of two molecules of carbon dioxide, water and hydrogen atom. This mechanism is responsible for the gelation.

![Fig. 8.1(a) FESEM image of the silica film prepared on Aluminium substrate](image-url)
8.3.2 Surface morphological studies

The two dimensional morphological studies of water repellent silica coatings have been carried out using FESEM micrographs as shown in Fig. 8.1 (a-c). Static contact angles of all substrates were above 150°. FESEM images of a top view of the coatings on different substrate shows that the surface is microscopically rough, which has a porous morphology [18]. The morphology of the films involves both micro and nano scale hierarchical structures. The nucleation and growth of the metal substrate influences the surface morphology of the prepared samples. Due to the porous morphology, it can be expected to show superhydrophobicity. In case of Copper and aluminium substrates, it is observed that the irregular shaped silica particles are non-homogeneously spread on the substrate to achieve the superhydrophobic nature.

Fig. 8.1(b) FESEM image of the silica film prepared on Brass substrate

8.3.3 Atomic force microscopy

The superhydrophobicity is also dependent on its surface topography. Figure 8.2 (a-c) shows the three dimensional atomic force microscopy images of the silica films on aluminium, brass and copper substrates respectively. The images were recorded at 1×1 μm² planar in contact mode. The surface of the films has many dispersed islands distributed on the film surface. Therefore, a silica coating on copper, aluminum and brass substrates gives higher contact angle values.
Fig. 8.1(c) FESEM image of the silica film prepared on Copper substrate

Fig. 8.2(a) AFM image of the silica film prepared on Aluminium substrate
Fig. 8.2(b) AFM image of the silica film prepared on Brass substrate

Fig. 8.2(c) AFM image of the silica film prepared on Copper substrate

8.3.4 Fourier transforms infrared spectroscopy

The chemical composition of the films deposited on aluminium, copper and bronze substrates were investigated by the FTIR spectroscopy using the KBr method in transmission mode. Several characteristic absorption peaks were observed in the range 450 to 4000 cm\(^{-1}\) indicating the presence of methyl groups in the sample. The FTIR
spectra of the silica films prepared with different metal substrates are shown in Fig. 8.3 (a-c), respectively.

The peak at 1122 cm\(^{-1}\) corresponds to the Si–O–Si asymmetric stretching vibration [19]. The presence of this peak confirms the formation of a network structure inside the film. The absorption band observed at around 2950 cm\(^{-1}\) are due to stretching of C-H bonds, the peaks observed at 1274, and 782 cm\(^{-1}\) are due to the Si-C bonds [20]. The broad absorption band at around 3400 cm\(^{-1}\) is due to the –OH groups [21]. The residual Si-OH groups are the main source of hydrophilic character. The intensity of the peak at 3400 cm\(^{-1}\) of –OH group is low as compare to the intensities of the C-H absorption peak at around 2950 cm\(^{-1}\) and Si-C absorption peak at around 782 cm\(^{-1}\). The Si-OH band seen in the FTIR spectra indicates that surface hydroxyl groups are still exist, even though the materials show the strong hydrophobic properties.

![FTIR spectra and contact angle images](image)

**Fig. 8.3** FTIR spectra and contact angle images of silica coating on different metallic substrates (a) aluminium substrate, (b) brass substrate and (c) copper substrate

### 8.3.5 Static and dynamic water contact angle measurements

The hydrophobicity of the resulting surfaces was assessed with water contact angle measurements. A low sliding angle renders the surface “nonsticky”, a property
that is crucial for the fabrication of water-repellent and self-cleaning surfaces. The Young's equation [22] for the contact angle ($\theta$) of a liquid droplet can be applied only to a flat surface and not to a rough one. The effect of surface roughness on wetting is accounted by the model developed by Wenzel [23], where it is assumed that the space between the protrusions on the surface is filled by the liquid. The apparent water contact angle ($\theta_{\text{rough}}$) and intrinsic water contact angle ($\theta_{\text{flat}}$) are then linked by,

$$\cos \theta_{\text{rough}} = r \cos \theta_{\text{flat}}$$

(8.5)

where $r$, is the ratio between the true surface area and its horizontal projection. This regime provides hydrophobic interfaces with contact angles below 120°; however, it cannot give rise to superhydrophobicity. In Cassie state, the apparent water contact angle ($\theta_{\text{rough}}$) is related to the intrinsic water contact angle ($\theta_{\text{flat}}$) of the solid surface by the Cassie–Baxter equation [24],

$$\cos \theta_{\text{rough}} = \psi_s \cos \theta_{\text{flat}} - (1 - \psi_s)$$

(8.6)

Where, $\psi_s$, is the area fraction of the solid surface that contacts water. From this equation, it is apparent that $\theta_{\text{rough}}$ is greater than 90° (or $\cos \theta_{\text{rough}} < 0$) if

$$\psi_s < \frac{1}{1 + \cos \theta_{\text{flat}}}$$

(8.7)

The Cassie–Baxter model assumes that a droplet is suspended on the rough structures and allows air trapping between the rough structures on a surface underneath the droplet. The Cassie–Baxter model suggests that the trapped air is a key for the superhydrophobic behavior. Sliding angle (SA) can be used to demonstrate the self-cleaning properties of superhydrophobic surfaces. Generally, superhydrophobic surfaces with SA less than 5° are needed for the self-cleaning property. The SA is the inclined angle at which the tailing edge of a drop of known mass will just begin to move and is a manifestation of the force required to dislodge a liquid from a surface. The maximum frictional force ($f_{\text{max}}$) required to dislodge a liquid from a surface can be calculated via the formula shown below;

$$f_{\text{max}} = mg \sin \theta$$

(8.8)
where, \( m \) and \( g \) are the mass of the water droplet and the acceleration due to gravity, respectively. Where \( \theta \), represents the minimal sliding angle of the water droplet on the hydrophobic surface.

This composite surface has a higher CA because of the air/liquid interface and can result in superhydrophobicity. Thus, Cassie-Baxter state is preferred rather than Wenzel state due to very small hysteresis and excellent rolling behavior even at tilting angles of a few degrees. The surface wettability for film prepared on various metal substrates was observed by CA and SA measurements before and after deposition, and a related CA and SA are listed in tables 8.1 and 8.2.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Contact angle</th>
<th>Sliding angle</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>before deposition ((\theta \pm 2)^\circ)</td>
<td>after deposition ((\theta \pm 2)^\circ)</td>
</tr>
<tr>
<td>Aluminium</td>
<td>69</td>
<td>164</td>
</tr>
<tr>
<td>Brass</td>
<td>58</td>
<td>153</td>
</tr>
<tr>
<td>Copper</td>
<td>61</td>
<td>161</td>
</tr>
</tbody>
</table>

Table 8.1: Comparisons of contact angle (CA) and sliding angle (SA) before and after deposition on of a various metal substrates with water

<table>
<thead>
<tr>
<th>Metal</th>
<th>Sliding angle ((\theta \pm 2)^\circ)</th>
<th>Maximum frictional force ( f_{\text{max}} ) ((\mu\text{N}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>7</td>
<td>11.94</td>
</tr>
<tr>
<td>Brass</td>
<td>5</td>
<td>8.54</td>
</tr>
<tr>
<td>Copper</td>
<td>3</td>
<td>5.12</td>
</tr>
</tbody>
</table>

Table 8.2: Maximum frictional force required to slide water droplet on the metal substrates after deposition
8.3.6 Effect of humidity and Chemical aging test

The stability of the water contact angle over time is a very important factor for superhydrophobic surfaces, providing information about the long-time surface dynamics. Unfortunately, results from long-time stability measurements are seldom reported [25]. Humidity is a measure of the amount of water vapours in the air. The relative humidity (H) is given by equation [17].

\[
H = \frac{e}{e_s} \times 100
\]  

(8.9)

Where, \(e\) is actual vapour pressure and \(e_s\) is saturated vapour pressure. In humid atmosphere, it may be mentioned that actual vapour pressure \((e)\) is always less than the saturated vapour pressure \((e_s)\). The effect of humidity on the wetting properties of silica film coated on different metal substrates were carried out at relative humidity of 95% at 35°C temperature over 90 days. It was observed that there was no any significant effect on the superhydrophobicity of the silica films. This reveals that the silica films prepared on metal substrates are strongly durable against humidity. The anticorrosive performance of the sol–gel coating was tested by direct exposure of the coated metal substrates to corrosive media. Interestingly, chemical aging test demonstrated that the superhydrophobic nature is maintained even though the deposited film was soaked for 100 h in 50% of HCl solution. However, we found that the water contact angle decreased by 10° to 15° after 120 h of exposure to the acid environment.
References