Silica–zirconia alkali-resistant coatings by sol–gel route

Sunetra Laxman Dhere*

Shri. S.H. Kelkar College of Arts, Commerce and Science, Devgad 416 613, India

Generally, to make the surface hydrophobic, silica-based coatings are preferred in various fields. When the coatings on glass or metal are exposed to alkaline surrounding, the silica network starts to deteriorate and its hydrophobic character ceases. To overcome this problem, we developed a silica-based coating along with zirconia which sustains the alkali attack and hydrophobicity is preserved. The chemicals involved in the synthesis were methyl tetraethoxysilane (MTMS), zirconium propoxide (ZP), methanol (MeOH) and acetyl acetone (Hacac) as a chelating agent for ZP, oxalic acid and ammonium hydroxide as acid and base catalysts respectively. A simple two-stage sol–gel method and deep-coating technique was employed to obtain the coatings. The hydrolysis time of MTMS was varied and its effect on wetting behaviour of the coatings was noted. The optimized coating was characterized by FTIR, EDAX, SEM, optical transmittance and wetting properties were studied. The water contact angle before and after exposure to alkali for bare silica and silica–zirconia coating was measured to be 120°, <10° and 100°, 93° respectively, showing improvement in the potency of coating in alkaline surroundings.

Keywords: Alkali-resistant coating, contact angle, sol–gel method, silica, zirconia.

MIXED-metal oxide systems are of special interest in developing the materials which exhibit properties differing considerably from the corresponding single components. Particular interest exists for the SiO_2–ZrO_2 system due to its properties such as hardness, chemical resistance in alkaline environment, wear resistance, etc.[1,2]. Different studies have demonstrated that SiO_2 coatings prepared by dipping enhance the corrosion resistance of stainless steel in acid medium[3]. However, the exposition of these coatings to alkaline environment provokes the quick degradation of the SiO_2 network with the consequent cessation in hydrophobic nature and hence the corrosion resistance of stainless steel. Different authors have demonstrated that the incorporation of ZrO_2 increases the alkaline resistance of the coatings[4–6]. As zirconia shows multifunctional properties, extensive methods have been explored to synthesize it, including precipitation[7], sol–gel[8], thermal decomposition[9] and hydrothermal treatment[10]. Among these, the sol–gel process is considered to be a promising method to produce homogeneous sols with modified physical–chemical properties. The main problem of preparing coatings of this composition is related to the amount of ZrO_2 that can be incorporated. The difficulty is to obtain homogeneous SiO_2–ZrO_2 mixed oxide without phase separation[11] and the low critical thickness of the coating that can be achieved. There are several studies that report the preparation of silica–zirconia films and the difficulty to obtain crack-free coatings thicker than 0.5 μm in a single layer[12–14]. Report regarding the preparation of SiO_2–ZrO_2 sols via acid catalysis containing up to 40% mol of colloidal ZrO_2 to produce hybrid glass-like coatings onto steel substrates by EPD and dipping is available[15]. Further, different routes of synthesis of thicker hybrid coatings with different SiO_2–ZrO_2 compositions via acid and basic catalysis by the sol–gel technique have been studied[16]. ZrO_2–SiO_2 binary mixed gel glasses were prepared via the sol–gel method using zirconium oxychloride as a precursor, and the influence of the Zr content and heat treatment on the refractive index was studied[17]. It is generally considered that zirconia is a bioinert material as zirconia ceramics scarcely possess the ability to induce bone formation in biological environment. However, recent studies have demonstrated the *in vitro* bioactivity of the plasma–sprayed and micro-arc oxidized zirconia coatings[18,19]. Recently, ZrO_2 coatings have been used as biomedical coating due to their good biocompatibility[20]. Incorporation of ZrO_2 into a SiO_2 matrix is known to improve the chemical resistance to alkaline attack[21,22], fracture toughness[23,24] and surface acidity of the materials[25,26]. In this study, we synthesized SiO_2–ZrO_2 coatings via sol–gel method and investigated their properties for alkali attack resistance.

Experimental

In order to study the alkali resistance due to zirconia in the silica coatings, the coatings were synthesized by the simple sol–gel route. The chemicals used for this synthesis were methyl trimethoxysilane (MTMS) (Sigma–Aldrich Chemie, Germany) as silica precursor, zirconium propoxide (ZP) as a zirconia precursor, methanol (MeOH) as solvent and acetyl acetone (Hacac) as a chelating agent for ZP (s.d. fine Chemicals Limited, Mumbai), oxalic acid and ammonium hydroxide as acid and base

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*e-mail: sunetradhere@gmail.com

catalysts respectively. All the reagents were used as received. Double-distilled water was used for the preparation of desired concentration of catalyst. Glass substrates (Blue Star, India) of 1.5 cm × 5 cm dimension were used in all experiments. To get uniform coatings, the glass substrates were cleaned by the procedure described earlier[27] and the volume ratio of MeOH : MTMS : ZP : Hacac : acidic H_2O : basic H_2O was optimized to be 5 : 2 : 0.5 : 1 : 1 : 1.

When ZP was added to MeOH, turbid solution or precipitation was observed. In the preparation of the mixed oxide system, it is crucial to avoid the precipitation of the metal oxide precursor possessing extreme water sensitivity. In the present work, Hacac was used as a chelating agent for the zirconia precursor. Half of the solvent was mixed with Hacac and used for diluting the zirconia precursor, while the remaining half was used for dilution of silica precursor. Before mixing the diluted silica and zirconia precursors, it is necessary to pre-hydrolyse the silica precursor. Oxalic acid (0.01 M) was added to diluted silica precursor and the pre-hydrolysis time of MTMS was varied from 0 to 3 h with constant stirring in steps of 0.5 h. The effect of pre-hydrolysis on the coatings was noted. Before addition of transition metal species the hydrolysis reaction should be completed so as all the water has been consumed. Otherwise the unreacted water could lead to precipitation of the transition metal alkoxide. This hydrolysed solution was added to the diluted zirconia precursor, which gave a clear yellowish solution. To this hydrolysed precusor mixture 3.5 M NH_4OH was added and stirred for about 15 min and allowed to stand. The obtained alcosol was then transferred to the test tubes and the cleaned glass substrates were immersed into it. This assembly was kept still and the substrates were held vertical till their withdrawal from the sol. As solvent evaporation affects the gelation taking place in due course of time, the test tubes were tightly wrapped.

Fourier transform infrared (FTIR) spectra were recorded in transmission mode to observe the chemical bonds in the coating material using spectrometer (Model No. 783, Perkin Elmer, USA). The morphology of the coatings was observed using field emission electron microscopy (FESEM). Energy dispersive analysis by X-rays (EDAX) of the sample was recorded to confirm the presence of zirconia in the coatings. The optical behaviour of the coating was studied by transmittance spectra obtained using UV–visible spectrophotometer (UV 1800, Shimadzu). The wetting behaviour of the coatings was determined by static and sliding contact angle measurements using a contact angle meter equipped with CCD camera (Ramehart Instrument Company, USA). The alkali attack resistance of the coatings was studied by dipping the samples in alkaline solution for a month and its effect on the wetting behaviour, roughness and optical properties was reported. The coatings were labelled as Z1, Z2, Z3 and Z4 prepared using 0, 1, 2 and 3 h pre-hydrolysed MTMS.

Results and discussion

Reaction mechanism

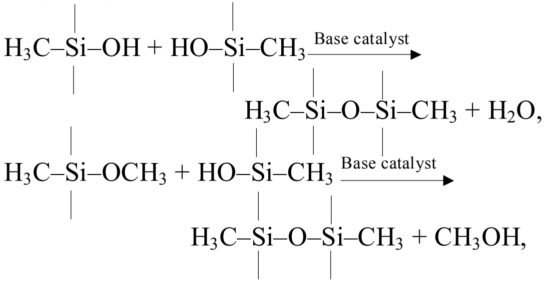
It has been well documented that the hydrolysis of silica precursor is slow in a neutral alcoholic solution and thus an acid or a base is needed to catalyse the reaction in the synthesis of SiO_2 by sol–gel process. With an acid catalyst, oxonium ions (H_3O^+) attach electrophilically to the oxygens of alkoxy groups (protonation), which makes the Si atoms highly prone to nucleophilic attack by water. With a base catalyst, a hydroxide ion (OH^-) nucleophilically attacks a positively charged Si atom. Unlike silicon alkoxids, most transition metal alkoxides, including ZP are quite reactive and hence special care must be taken to prevent direct hydrolysis by moisture. For this purpose Hacac was used in the synthesis, as mentioned in the experimental part. The vast difference in hydrolysis reactivity between silicon alkoxide and transition metal alkoxides has been addressed in the literature using a partial charge model (PCM)[28]. Accordingly, the reactivity between $M(OR)_4$ (M = metal) and HOX (X = H or R) depends mainly on the electrophilic power (determined by partial charge $\delta(M)$) and unsaturation of the metal atom (determined by N–Z, where N and Z are the usual coordination number and oxidation state of the metal respectively). Due to low electronegativity, the silicon atom in silicon alkoxide has a relatively low electrophilic power. This low value of $\delta(M)$ and zero value of N–Z make silicon alkoxides fairly stable against hydrolysis in comparison to transition metal alkoxides such as zirconium propoxide[29]. Therefore, we need to add acid or base catalyst to initiate the hydrolysis and condensation reactions in case of mixed metal oxide system. In this study, we used 0.01 M oxalic acid as a hydrolysing agent and ammonium hydroxide as catalyst for condensation reactions. The reactions taking place in the sol are as follows

Hydrolysis:

$$CH_3\text{–}Si\text{–}(OCH_3)_3 + 4H_2O \xrightarrow{\text{Acid catalyst}} CH_3\text{–}Si\text{–}(OH)_3 + 3CH_3OH,$$

$$Zr\text{–}(OC_3H_7)_4 + 4H_2O \xrightarrow{\text{Acid catalyst}} Zr\text{–}(OH)_4 + 4C_3H_7OH.$$

Condensation:



$$H_3C\text{–}Si\text{–}OH + HO\text{–}Si\text{–}CH_3 \xrightarrow{\text{Base catalyst}} H_3C\text{–}Si\text{–}O\text{–}Si\text{–}CH_3 + H_2O,$$

$$H_3C\text{–}Si\text{–}OCH_3 + HO\text{–}Si\text{–}CH_3 \xrightarrow{\text{Base catalyst}} H_3C\text{–}Si\text{–}O\text{–}Si\text{–}CH_3 + CH_3OH,$$

$$\equiv \mathrm{Zr{-}OH} + \mathrm{HO{-}Zr} \equiv \xrightarrow{\text{Base catalyst}} \equiv \mathrm{Zr{-}O{-}Zr} \equiv + \mathrm{H_2O},$$

$$(\mathrm{H_7C_3O})_3\mathrm{{-}Zr{-}(OC_3H_7)} + \mathrm{HO{-}Zr} \equiv \xrightarrow{\text{Base catalyst}}$$

$$\equiv \mathrm{Zr{-}O{-}Zr} \equiv + \mathrm{C_3H_7OH}.$$

FTIR studies

It is well known that the FTIR spectrum of a material provides information regarding the chemical bonds in the material. The chemical composition of the Z4 coating with 3 h pre-hydrolysis time for MTMS was investigated using FTIR spectroscopy with KBr in transmission mode. Several characteristic absorption peaks were observed in the range 450–4000 $\mathrm{cm^{-1}}$, indicating the presence of organic groups as well as Si–O and Zr–O bonds in the sample. Figure 1 shows the FTIR spectrum of Z4 coating. The broad absorption peak near 3600 $\mathrm{cm^{-1}}$ corresponds to low concentration –OH bonds which can be related with adsorbed water on the coating material, whereas the molecular water band appears at around 1640 $\mathrm{cm^{-1}}$. This is the water used in the synthesis of coating material in the form of acid and/or base catalysts. The absorption peaks at 2867 and 2968 $\mathrm{cm^{-1}}$ are assigned to strong bonds of $-\mathrm{CH_3}$ groups. These are from the unhydrolysable methyl groups in the MTMS precursor. These $-\mathrm{CH_3}$ groups are non-polar and serve as a water-repellent moiety in the coating material. A peak observable at 1534 $\mathrm{cm^{-1}}$ corresponds to the complex of Zr with Hacac[29]. Being in complex form, the whole ZP may not get consumed in the hydrolysis and condensation reactions[30]. The strong Si–O–Si asymmetric stretching vibration peak is visible near 1100 $\mathrm{cm^{-1}}$ (ref. 31). The presence of this peak confirms the formation of a silica network structure in the coating material. It has been reported that the Si–O–Si stretching band[32] near 1100 $\mathrm{cm^{-1}}$ shifts towards lower values when Zr atoms replace the Si atoms to form Si–O–Zr hetero-linkages[26]. Therefore, the absorption peak at 990 $\mathrm{cm^{-1}}$ assigned to the Si–O–Zr cross-linkage confirms the cogelation. The sharp peak at around 780 $\mathrm{cm^{-1}}$ is reported for Si–C bond of unhydrolysable $-\mathrm{CH_3}$ in MTMS. As the intensity of this peak is also high, the hydrophobic character of the coatings can be attributed to this chemical bond.

Energy dispersive analysis by X-rays

Again to confirm the presence of Zr in the coatings, EDAX was carried out. This is a characterization technique used to detect the elements present on the surface of thin films. The probed electron beam strikes the atoms on the surface and knocks out the inner shell electrons. The transition of electrons from higher energy orbital to fill the vacant spots of the knocked out electrons in the inner shell is in the form of characteristic X-rays. EDAX of Z4 coating is shown in Figure 2. The peaks centred at 1.8 and 2 keV correspond to Si and Zr respectively. This confirms the presence of Zr in the coating.

Surface morphological studies

The gelation time of mixed oxide sol was observed to be prolonged. Since the rate of reaction was lowered, smaller sized particles were formed. From the field emission scanning electron (FESEM) images, it can be seen that the surface is quite uniform and smooth except shallow cracks or busted bubble-like microstructures (Figure 3 *a* and *b*). No interesting surface microstructure is seen for any of the coatings. The shallow cracks and busted bubble–like shapes seen on the surface can due to be the evaporation of solvent while heat-treating the sample. Further, the contact angle measurements showed that even though the coatings were non-wetting they were

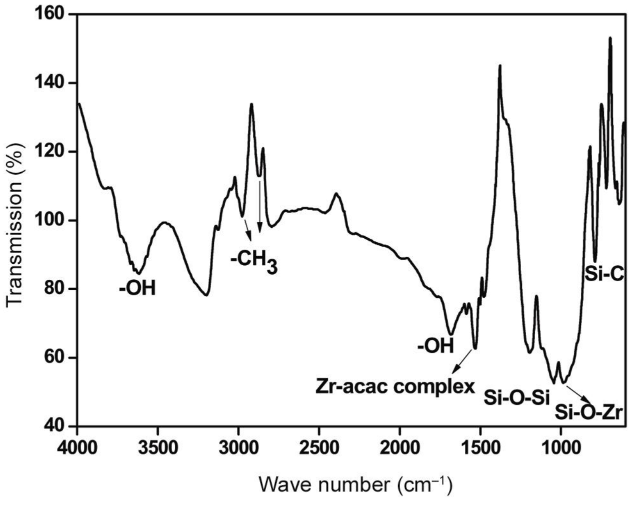


Figure 1. Fourier transform infrared spectrum of Z4 coating.

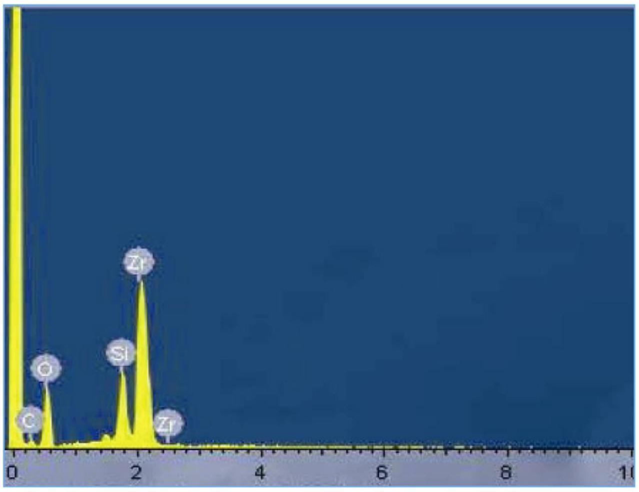


Figure 2. Energy dispersive analysis by X-rays of Z4 coating.

not superhydrophobic. The absence of microstructures and hence low roughness can be a probable cause for the observed values of contact angle.

Optical studies

The gelation time of mixed sol prolonged with increase in pre-hydrolysis time of MTMS. Since the rate of reaction was lowered, smaller sized silica particles were formed and hence higher transparency of the coatings, was expected. For optically transparent coatings, roughness should be lower than the wavelength of visible light (380–760 nm)[33]. From the optical transmission curves obtained for Z4 and Z1 (Figure 4 *a* and *b*), it is clear that the Z4 coating is more transparent than the Z1 coating. The optical transmission for Z4 is about 91%, while that for Z1 coating is 84%. The hydrolysis time of Z4 coating was 3 h, which is optimum for complete hydrolysis, thus assuring the moderate rate of gelation. This gives rise to the formation of smaller sized particles. From the surface profiler study also, the roughness value for Z4 coating was confirmed to be 208 nm, which is lower than the wavelength of visible light, making it more transparent to the visible range.

Contact angle measurements

Water contact angle measurements provide information regarding the wetting behaviour of the silica–zirconia coatings. The contact and sliding angles for Z4 and Z1 coatings are shown in Figure 5. The 8 μl water droplet was placed on the zirconia–silica coating prepared with 0 and 3 h pre-hydrolysis of MTMS. The static water contact and sliding angles for Z4 coating are 120° and 20° respectively, while for Z1 coating they are 100° and 30° respectively. The static water contact angle and sliding angle values for Z2 and Z3 lie intermediate to those of the Z1 and Z4. Water drops were seen to effortlessly slide off the coatings at the mentioned sliding angles without leaving traces of water on the surface. It is generally assumed that a surface can be termed as hydrophobic if the contact angle of water is greater than 90°. In the present work, the value of contact angle is not high, but the coating shows excellent non-wetting behaviour. The low roughness of the surface could help the water drops to slide off the surface.

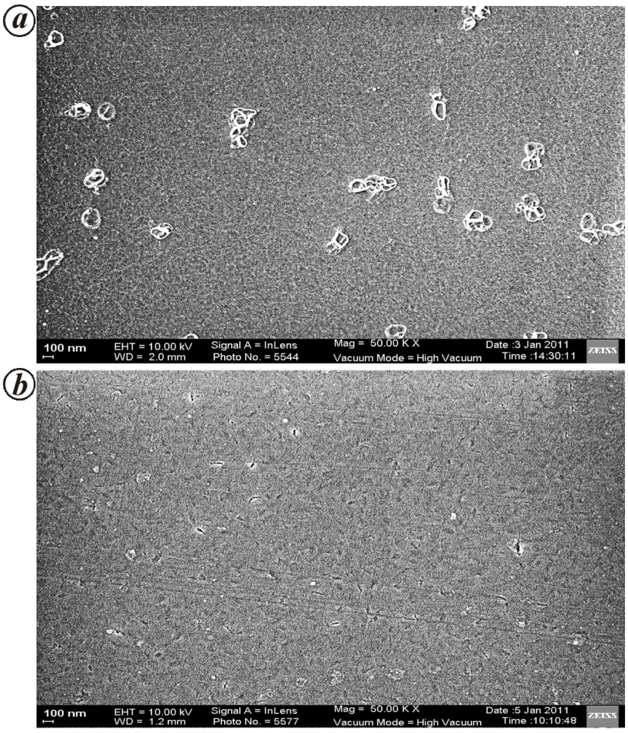


Figure 3. Scanning electron microscopic images of (***a***) Z4 and (***b***) Z1 coatings.

Alkali resistance of silica–zirconia coatings

Zirconium owes its chemical resistance to the dense, stable and inert nature of zirconia. As zirconia is known to be a good candidate for chemical resistance, more specifically, alkali attack resistance, the sol–gel synthesized silica–zirconia coatings were tested for alkali attack resistance. A strong alkali NaOH and a weak alkali NH_4OH were chosen to study the alkali resistance of the coatings. 1 M solutions of NaOH and NH_4OH were prepared and bare silica (MTMS-based coating) and silica–zirconia (Z4)-coated glass substrates were immersed in the alkaline solution. These coatings were immersed in the alkali bath for a whole month and the containers were wrapped tightly. After a month, the samples were taken out from the alkali baths and their wetting behaviour and optical

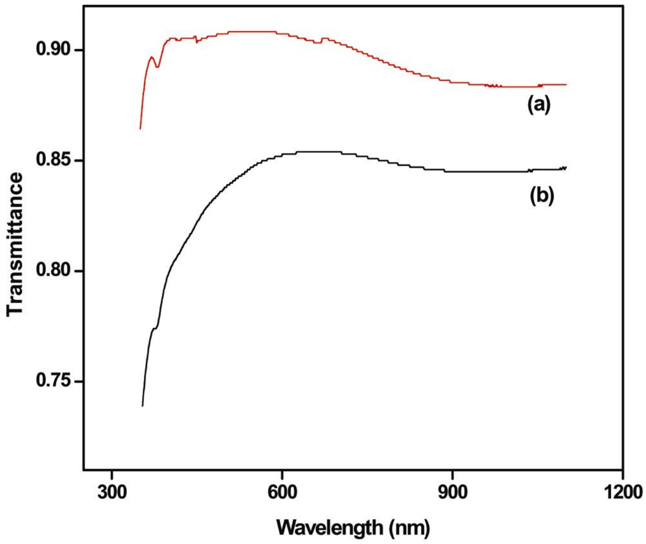


Figure 4. Optical transmittance spectra for (a) Z4 and (b) Z1 coatings.

Table 1. Comparison of alkali attack resistance of bare SiO_2 and SiO_2-ZrO_2 (Z4) coatings

			After immersing in alkali			
	Before immersing in alkali		1 M NH_4OH		1 M NaOH	
Coating	Contact angle (degree)	Optical transmission (%)	Contact angle (degree)	Optical transmission (%)	Contact angle (degree)	Optical transmission (%)
SiO_2	120	75	<20	62	<10	59
SiO_2–ZrO_2	100	85	97	82	93	80

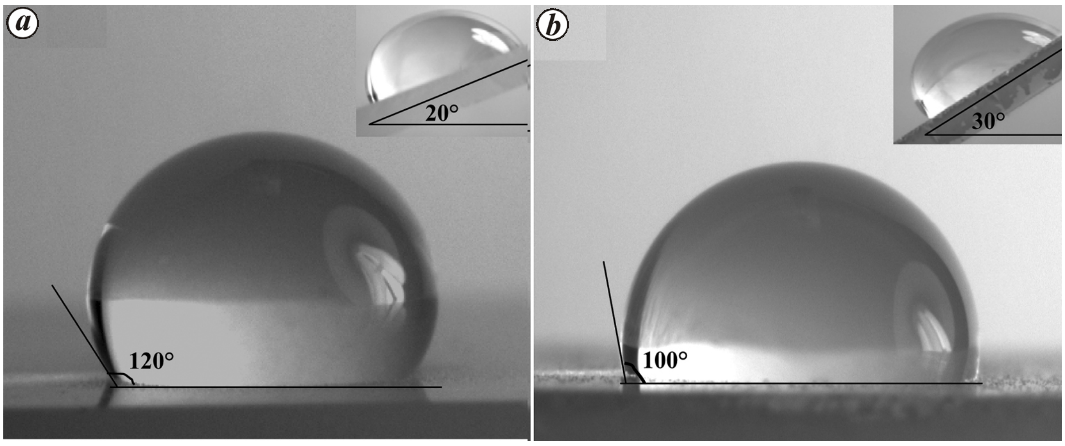


Figure 5. Static water contact angle images of (***a***) Z4 and (***b***) Z1 coatings. (Inset) Sliding angle image.

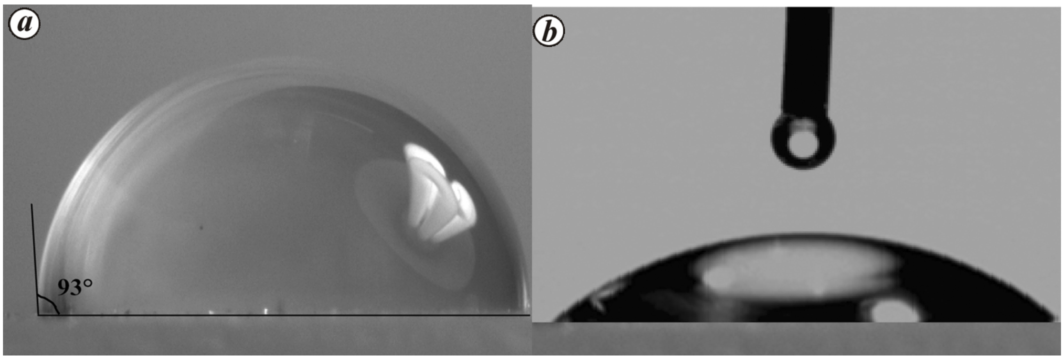


Figure 6. Static water contact angle images of (***a***) Z4 and (***b***) bare silica coatings after immersing in strong alkali.

transmission were noted. It was observed that the bare silica coatings were washed off completely in strong as well as weak alkaline solutions making the substrate whitish and less transparent, whereas the silica–zirconia coating was seen to be intact in weak as well as strong alkali solutions. The results presented in Table 1 show the change in optical transmission and static water contact angle before and after alkali attack test. The measured contact angle images are presented in Figure 6. The water contact angle for bare silica and silica–zirconia coatings before and after exposure to alkali are 120°, <10° and 100°, 93° respectively. For the bare silica coating the water drop was seen to spread onto the substrate as soon as it was dropped. The hydrophobic character shown by bare silica coating was completely lost, while that of silica–zirconia coating persisted.

Conclusions

In order to make the silica coatings alkali-resistant, zirconium propoxide was added to the sol. The coatings were synthesized by a simple sol–gel route. In order to obtain good-quality coatings, the volume ratio of MeOH : MTMS : ZP : Hacac : acidic H_2O : basic H_2O was optimized at 5 : 2 : 1 : 1 : 1 : 1. As the hydrolysis time of ZP and MTMS is different, the pre-hydrolysis of MTMS was carried out. The effect of pre-hydrolysis of ZP on the physico-chemical properties of the coatings was studied. The silica–zirconia mixed oxide coatings are non-wetting and water slides off easily without leaving any trace on the surface. The optical transmission was observed to be improved for the 3 h pre-hydrolysed ZP coating. The mixed oxide coatings were observed to be intact when kept immersed in strong and weak alkali, while the bare silica coatings though more hydrophobic were seen to get washed off and water contact angle was reduced.

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