Chemomechanical effects in optical coating systems

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Abstract:
The major in-service failure mechanisms of modern optical coatings for architectural glass can be mechanical (e.g. scratch damage). Many of these coatings are multilayer structures of less than 100nm thickness and different coating architectures are possible (i.e. different layer materials, thickness and stacking order). These coatings are exposed to different types of climatic conditions. In such circumstances it has been shown that chemomechanical effects can lead to changes in the hardness as well as the fracture resistance of bulk oxides. High performance glass is coated with anti-reflection coatings (e.g. ZnO, SnO₂) and barrier layers (e.g. TiOₓNᵧ) which are also expected to suffer from such chemomechanical effects. In this study we have demonstrated the chemomechanical behaviour of a range of optical coatings exposed to water. Water exposure tends to reduce the hardness and, because of this plasticising effect, increase the fracture resistance of the coating making it more vulnerable to plastic deformation during scratching. The susceptibility of different coatings to chemomechanical effects is discussed.

Keywords: Chemomechanical effects, Scratch damage, and Optical coatings.

1. Introduction
The use of optical coatings on glass has been on the rise, as glass itself nowadays cannot fulfil the requirements of many applications on its own. Glass has become an integral part of human life as most modern buildings use a large amount of glass, much of which is coated to improve energy efficiency. Coated glass is used in many other applications such as lenses and other optical elements. Transparent coatings
such as ZnO, TiO\textsubscript{2}, SnO\textsubscript{2}, and ITO are a few of the oxide coatings which are used to coat the glass for various purposes such as anti-reflection coatings or barrier layers.

The environment, especially water, is known to have a considerable effect on the surface mechanical properties of many materials such as ceramics and oxide films. [1-6]. Water exposure tends to reduce the hardness and, because of this plasticising effect, increase the fracture resistance of bulk oxides and coatings making them more vulnerable to plastic deformation during scratching [7]. This effect has been known for many years but its significance for many optical coatings has not been completely realised [6]. Such chemomechanical effects may be of particular importance for oxide coatings in cases where the chemistry of the environment can induce changes in mechanical properties which in turn affect their wear resistance [8]. The effects of the environment usually involve a chemical reaction - rate controlled wear process in which either the oxide or water softened layers can be easily removed [9-11]. Even though the effect of moisture on fast fracture and slow crack growth is well known [7], attempts to convincingly demonstrate that plasticity and indentation hardness are also sensitive to the atmosphere (which is called the Rehbinder effect) were not very convincing until the advent of nanoindentation techniques. It has also been suggested [1] that Rehbinder effects could apparently occur in metals in situations where the properties of the substrate metal crystal were strongly influenced by the presence and mechanical properties of an oxide film. This is because the hardness of the oxide film itself, and hence its resistance to dislocation motion, could be influenced by an adsorbate.

Many workers have proposed mechanisms for chemomechanical effects [1, 5, and 12] but it is not certain which mechanisms are valid and which will occur in any given system. The best current explanation comes from models which consider the electronic interactions between dislocations and adsorbate-affected surfaces whereby the electronic energy levels associated with the disturbed material in the core of a dislocation will interact with the distorted band structure of the adsorbate-affected near-surface layer resulting in changes to dislocation mobility [1, 5]. Bending of the near-surface energy bands is expected and the more pronounced this effect, the greater the change in dislocation mobility. Though chemomechanical effects are well-known, relatively little work has been done on multilayered coating systems.
comprised of oxide coatings. In this paper we will discuss the chemomechanical effects observed in the component layers of solar control coatings and indicate how the chemomechanical behaviour of an oxide film present within this coating stack can influence the hardness of the whole system.

2. Experimental
A range of float glass samples with different single and multilayer coatings deposited by magnetron sputtering on the air side (by Pilkington Technical Ventre) were supplied in the form of 150mm square plates with a substrate thickness of 4mm. These coatings consist of the main oxide layers present in a typical solar control coating; the active layer is ~10nm silver surrounded by oxide anti-reflection (ZnO and SnO$_2$) and barrier coatings (TiO$_2$). Four different sample types were used:
1) Glass/TiO$_2$ (400nm thick top layer)
2) Glass/TiO$_2$/ZnO (400nm thick top layer)
3) Glass/TiO$_2$/ZnO/Ag/ITO/ SnO$_2$ (400nm thick top layer) and
4) Glass/TiO$_2$/ZnO/Ag/ITO /SnO$_2$/TiO$_2$ (Full solar control architecture, total thickness ~100nm)

The multiple layer coatings with the final layer of 400nm were deposited onto the same underlayer structure that is used in the full coating stack in order to minimise the microstructural differences in the coatings on the different samples.

The samples were ultrasonically cleaned using IMS immediately prior to testing and care was taken to keep the samples as clean and dry as possible. For each coating material, one sample was simply cleaned and dried, a second sample was soaked with water on the coated surface for 24hrs, a third set of experiments was performed on samples whose surface were soaked with water for 1hr and a fourth set of experiments was performed on samples with a thin film of water on their surface during indentation testing. The final set of samples were soaked with industrial methylated spirit (IMS) on the surface for 24 hrs to displace any water.

Microindentation and Nanoindentation experiments were performed on each set of samples with loads varying from 5N to 1mN using a Shimadzu microhardness tester and Nano Indenter II (Nano instruments Inc, Knoxville, TN, USA). The
Microhardness tests were performed under standard conditions (15s dwell time, laboratory air, 60% RH), and the loads used were 5N, 3N, 2N, and 1N. The measurements of the indentation dimensions and crack lengths were made with the optical system of the microhardness tester. Nanoindentation experiments were performed by making 50 indents with a general purpose Berkovich indenter (tip end radius 200nm); 10 indents were made at each load and each indent was placed 50 µm apart. The peak loads used were 500, 100, 10, 5 and 1 mN. The loading rate was 500 µN/s in all cases. There was some cracking observed in the water soaked samples on the surface and care was taken to ensure that the indentations were far enough apart to avoid interaction of the cracking. All the nanoindentation experiments on the different treated samples were performed using the same procedure.

Microindentations were imaged using a reflected light microscope while the nanoindentations were imaged using an E-SEM (Environmental scanning electron microscope) which is less susceptible to charging so the samples could be viewed uncoated and contaminated with water. It is known that the chemomechanical effects are caused mainly by the surface adsorbates and for oxides this effect is caused mainly by adsorbed water [5] – no attempt was made to clean the surface of any water residues prior to microscopic analysis. Energy dispersive x-ray microanalysis was used to monitor compositional changes caused by the water to the surface layers and check for the removal of any coating.

4. Results and Discussion

The microhardness results and nanoindentation load displacement curves clearly show differences for the different test series used. In this section the differences between the normal unaffected samples and the chemomechanically affected samples are discussed as a function of test load (and hence contact scale).
4.1 Microhardness testing
From Fig.1 (a) it is very clear that after soaking the surface with water for 24hrs there is a statistically significant drop in the hardness when compared to the dry sample, whereas this effect is not seen when the surface is soaked with IMS. Since it was evident from the microhardness testing that there is significant change in the surface properties of the coatings after soaking with water for 24hrs, and not much effect was found for the samples soaked in water for 1hr, with water on the surface and the samples soaked with IMS we performed nanoindentation tests on the samples soaked with water for 24hrs to see the effects at lower loads.

![Graph](image1.png)

Figure 1: The effect of environmental exposure at different times on the microhardness of the full coating stack (a) water and (b) IMS.

4.2 Nanoindentation tests
The effects of water on the full coating stack was clearly seen with microhardness testing hence we wanted to see the behaviour of this sample under lower loads, but in addition we performed tests on individual layers within the full coating stack to check for any differences in chemomechanical behaviour between them.
4.2.1 Solar Control Architecture (Glass/TiO$_2$/ZnO/Ag/ITO/SnO$_2$/TiO$_2$)

Figure 2: Comparison of the load-displacement curves for a full multilayer solar control coating tested dry and soaked in water for 24 hrs at loads (a) 500mN, (b) 100mN, (c) 10mN, (d) 5mN and (e) 1mN.

From Figure 2(a) (b) & (c) the load-displacement curves for all these samples have the same appearance, this confirms in both normal and water soaked samples there is not a large difference in mechanical properties but there is evidence of slight
chemomechanical softening as the maximum penetration depth for the soaked samples is greater. As the loads decrease, we can see from Figure 2 (d) & (e) that there is an initial offset of around 15nm; this is consistent with the indenter contacting and penetrating a soft surface layer. This behaviour was seen for water soaked samples but not for the samples soaked with IMS. Since the full coating stack is only around 100nm thick, it is clear that there is a significant effect on the top surface of the samples.

![Figure 3a](image1.png) ![Figure 3b](image2.png)

Figure 3: Scanning electron micrographs of a 500mN indent in the full coating stack sample tested (a) dry and (b) after soaking in water for 24h.

Figure 3a shows a typical 500mN indent in the glass with the complete coating stack. Radial cracks following the indenter edges and picture frame cracks are visible as is often observed when the indent depth is considerably greater than the coating thickness. For the water exposed sample (Figure 3(b)) we can still see picture frame cracks appearing but these are decorated by round balls which appear to be some kind of residue caused by exposure of silver within the coating stack to the atmosphere and water due to the cracking. EDX analysis indicates that this residue is most likely to be silver sulphide and is therefore formed due to reactions with the atmosphere after nanoindentation testing, rather than with the water during exposure. This indicates that the cracking penetrates at least to the silver layer. The chemomechanical softening has reduced the surface hardness which leads to an increase in picture frame cracking due to an increased bending of the coating into the impression created by plastic deformation of the substrate. This is a case where chemomechanical effects increase fracture, unlike what is generally observed for bulk oxides [7].
4.2.2 TiO$_2$ (400nm thick top layer) sample

Figure 4: (a) Chemomechanical effects in the load-displacement curves of a TiO$_2$ coating at 10mN peak load (b) Comparison of the hardness for TiO$_2$ coated sample in dry and wet conditions.

From Figure 4(a) it can be clearly seen that there is an initial displacement of about 40nm consistent with the indenter contacting and penetrating a soft surface layer. But this phenomenon is observed only at a very low load indicating rather than the whole oxide layer being affected by the surface adsorbates it is only the top part which is showing the characteristic chemomechanical effect. This is even more visible in Figure 4(b) where we can clearly see that at higher loads the difference in hardness is minimal but at lower loads there is clear reduction in hardness.
4.2.3 ZnO (400nm thick top layer) sample

Figure 5: Comparison of load-displacement curves for the 400nm ZnO coated sample tested dry and soaked with water for 24 hrs at loads (a) 500mN, (b) 100mN, (c) 10mN, (d) 5mN and (e) 1mN.
Unlike the other two samples tested we can clearly see that by soaking the ZnO sample with water for 24hrs has a large effect on hardness even at high loads (Figure 6); in this particular sample the presence of a soft layer is seen at 500mN load. Zinc oxide is hydrated very easily, exacerbating the chemomechanical effects [1].

![Graph showing hardness vs load for ZnO coated sample in dry and wet conditions.](image)

**Figure 6** Comparison of the hardness for the 400nm ZnO coated sample in dry and wet conditions.

The reduction in hardness of at high loads clearly indicates that the softening penetrates deeper into the sample when compared to TiO$_2$ where the change in hardness was occurring only at the lowest loads. This phenomenon may due to the susceptibility of ZnO to chemomechanical softening or it may indicate that the coating has an open columnar structure which allows water penetration and adsorption along boundaries promoting chemomechanical effects deeper in the material. The ZnO is the only crystalline layer in the coating stack and atomic force microscopy indicates it is rougher than the TiO$_2$ layer which implies that the later explanation is more likely.
4.2.4 SnO$_2$ (400nm thick top layer) samples

Figure 7 shows that there are no significant chemomechanical effects in the SnO$_2$ coating even at lowest loads used in this study.

Figure 7: Comparison of the hardness for SnO$_2$ coated sample in dry and wet conditions.

(a) Defects in the surface
(b) Coating detachment
(c) Blister in the coating
(d) Appearance of cracks

Figure 8: SEM micrographs of the indentations in the 400nm SnO$_2$ coated sample (a) before soaking in water and (b) after soaking with water for 24hrs. (c) Cracks and blisters on the surface after soaking with water for 24 hrs and (d) detachment of the SnO$_2$ coating at the interface with silver.
Figure 8 (b) shows that some detachment of the SnO$_2$ coating occurred at loads of 1mN and above; in this case there was not much effect on the surface hardness, but the visible damage was far more than for the other coatings. The reason for this is due to the penetration of water through the cracked coating weakening the interface with lower layers within it. This occurs without indentation damage and is visible in the blistering observed after 24 hours exposure to water (Fig 8c). EDX indicates the failure occurs at or near the ITO/Ag interface.

4.2.5 Comparisons between single layer coatings and the multilayer stack.

Comparing the 10mN load-displacement curves for the full solar control coating stack (Figure 2 (c)) with the TiO$_2$ (Figure 4(a)) and ZnO (Figure 5 (c)) thick single layer coatings, it can be seen that the size of the chemomechanical effect, as determined by the difference in the displacement at maximum load between wet and dry surfaces is greatest for the ZnO coating (~90nm) followed by the TiO$_2$ (~45nm) and least for the full coating stack (~20nm). There is no apparent chemomechanical effect in the SnO$_2$. In the multilayer stack the top layer of TiO$_2$ is only ~10nm thick and the layer immediately beneath it is SnO$_2$ so it is not surprising that the full stack shows a lower chemomechanical response. The interface between ITO and silver is attacked by water if this can penetrate through the upper layers of the coating.

Whilst the outer TiO$_2$ layer acts as a barrier to water penetration the mechanical performance of the coating is reasonable. However, if water can diffuse to the ITO/Ag interface or through to the ZnO anti-reflection layer serious mechanical damage to the coating is likely. This highlights the need for a good barrier layer if these optical coatings are to be exposed to the atmosphere during handling or service.

Conclusions

1) The chemomechanical behaviour of a range of oxide coatings has been tested and different results have been seen with some materials showing strong effects (ZnO), some smaller effects (TiO$_2$) and some no effects at all. The relatively large effect seen in the multilayer stack implies that water has penetrated through the outer layers of the coating to the buried ZnO layer.
2) All the tested samples which show a chemomechanical effect possess soft surface layers after soaking in water.
3) There has been a considerable physical damage (blistering/chipping) occurring on the tin oxide coated sample due to water reactions with the layers below the thick outer coating.
4) There is a deposit decorating the picture-frame cracks on the full stack coating which is due to the silver present within the coating stack. Chemomechanical softening has led to enhanced picture-frame cracking in the coated samples.
5) Chemomechanical effects cannot be ignored if ZnO and TiO$_2$ coatings are to be used in aqueous environments.

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References
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