Preparation of functional coatings for display glass applications by sol-gel derived techniques

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Thin glasses are very important for display applications. If high bending strength is required, state-of-the-art technologies cannot be applied due to the small thickness. SiO_2 coatings derived from tetraorthosilicate and also from a methyl modified silane in combination with a nanoparticulate silica sol are applied to 0·5 mm thick soda-lime glasses by dipping and are fired at 500°C. The bending strength of the glass (double ring method) is increased from about 450 MPa to 1100 MPa by a combination of filling and clamping of the micro flaws in the glass surface. An organic-inorganic coating of only 10 µm in thickness is introduced, which can protect 2 mm thick floatglass with extremely high bending strength (600 MPa) completely against the mechanical load of a sand falling test, whereas the bending strength of uncoated float glass is decreased down to 10 % of its initial value by this test. In addition, coatings with optical functions, useful for display applications like antireflective properties, NIR reflectance or colour neutral absorbance of visible light for contrast enhancement, are introduced briefly.

Thin glass is of high importance for display glass applications. Therefore, it is an important aim for research and development to increase the functionality and simultaneously to save processing steps and to decrease the costs. For this, wet chemical sol-gel derived coatings and especially nanoparticulate systems can be an interesting tool. This hypothesis will be proven in this paper by the description of coatings which can increase and preserve the bending strength of thin glass. In addition, functional coatings for contrast enhancement and antireflective applications will be introduced briefly.

It is well known that the practical bending strength of glass products is much smaller than it's theoretical one. This is due to micro flaws in the surface near region of the glass.(1) These micro flows also lead to static fatigue depending on the load and the environmental conditions.(23) The-state-of-the-art technology for increasing the bending strength of glass products is the generation of compressive stresses in the glass surface near region by alkaline ion exchange(4–7) or by tempering.(8) In both cases, the zone of compressive stress is in a depth of typically 50–150 µm, which is too deep for thin glass application. Furthermore, tempering of thin glass seems to be very difficult with respect to deformation and ion exchange is not possible in alkaline-free display glasses.

Fabes & Uhlmann have shown that sol-gel derived SiO_2 coatings could increase the bending strength of silica glass rods by a factor of 2 and explained this effect by filling the micro flaws at least partially (decrease of flaw length).(9,10) Maddalena & Guglielmi(11) could increase the bending strength of soda–lime–silica glass plates by SiO_2, SiO_2–ZrO_2 and ZrO_2 coatings. Schmidt *et al*(12) could obtain a 4-fold strength increase by coating soda-lime glass with multicomponent multilayer glass coatings. It has been shown already, that state-of-the-art SiO_2 coatings(13) in combination with 6 µm thick SiO_2 coatings derived from methylsilane modified colloidal silica sols(14,15) on the edges of cutted glass could increase the bending strength of cutted glass bars (3 point bending test) by a factor of 2. It was shown(16) that this effect can be attributed to a partial flaw healing in combination with a "clamping" of the flaws by the thick SiO_2 coating.

Therefore, it was interesting to apply these coatings to thin glass in order to investigate to what extend the strength of this glass could be increased.

The next question was how to preserve this state of high strength against mechanical attack. It was obvious that glass-like coatings on glass would be damaged by mechanical attack in the same way as the glass itself due to perfect chemical bounding and similar elastic moduli and could therefore never preserve the strength. On the other hand side, organic polymer coatings, which have been developed especially for container glass applications,(17–23) have thicknesses in the range of 50 µm.(24) This is not very suitable for display glass applications which claim for minimized thicknesses. Therefore, an organic-inorganic coating, which had been developed for the protection of glass bottles against the mechanical damage caused by bottle-to-bottle contact at a bottling plant(25,26) was applied to float glass (2 mm) as demonstrator for the protection of this thin coating (10 µm) against the mechanical load of a sand falling test.

As a third approach to thin glass with improved mechanical properties, ZrO_2 coatings are applied and their scratch hardness was investigated in comparison

*now with Topac Multimedia GmbH, Güthersloh to chemical toughened glass. Finally, additional optical functions like absorbance for contrast enhancement and antireflective coatings with good durability are described briefly.

Experimental

For the investigation of the bending strength increasing coatings, soda-lime silicate glass plates of 10 cm × 10 cm × 0·5 mm size were used. Before coating, the glass plates were cleaned using a lab dishwasher at 70°C with an alkaline cleaner.

A low viscous SiO_2 coating sol (TEOS-sol) was prepared from tetraethoxysilane (TEOS) according to References 13, 16 using a TEOS:H_2O:EtOH =1:2:2 mixture and HCl (pH=2) for hydrolysis (25°C, 3 h). The coating sol for the thick SiO_2 coatings (MTKS-sol) was prepared according to References 14–16 using TEOS, methyltriethoxysilane and colloidal silica sol (Levasil, BAYER) in a molar ratio of 1:3·7:1·5 and HCl (pH=1·5) for hydrolysis (3 h, 25°C). The coatings were prepared by dipping with a withdrawal speed of 4 mm/s. After drying at 100°C for 30 min, the coatings were fired at 500°C for 1 h. The bending strength was measured by double ring bending test[27] using 25 samples each and evaluated according to Weibull statistics.

For the demonstration of the strength preserving effect, glass substrates of 10 cm × 10 cm × 2 mm were used and cleaned as described above. The coating sol (GAMAL-sol) was synthesized according to References 26, 16 using a prehydrolised epoxy functionalised silane and a prehydrolised aminosilane in combination with acetanhydrid for sol stabilisation. Furthermore, a small amount of aluminium-sec butylate was added for the promotion of the organic cross linking.[26] The coatings were prepared by dipping (5 mm/s) and were cured at 120°C for 10 min.

Double ring bending test with Weibull statistics was performed[27] with coated and uncoated samples before and after sand falling test[28] by sprinkling 500 g Al_2O_3 powder (grain P30) from a height of 1·5 m to the rotating glass substrate (impact angle 45°).

The ceramic coatings (ZrO_2) for improving the scratch hardness were applied to 3 cm × 3 cm × 2 mm samples of chemically toughenable (but untoughened) special glass (Corning). The sol was synthesized from Zr-isopropylate using a standard synthesis route.[13]

Results and discussion

Strength increasing coatings

The bending strength of the coated and uncoated thin glass was characterised by the double ring bending test, although, according to German standards[27] a minimum glass thickness of 4 mm is demanded in order to exclude the influence of membrane stresses on the bending strength. However, since the double ring bending test and the Weibull statistics are a very good tool for the comparison of the different coatings, the influence of membrane stresses shall be neglected in first approximation. The results of the bending strength measurements are presented in Figure 1.

Figure 1 clearly shows that the uncoated samples have a bending strength of about 434 MPa and also a rather low Weibull coefficient of only 3·4, which indicates a rather broad distribution of flaw dimensions. The thin SiO_2 coating with the low viscous TEOS-sol leads to almost double bending strength (749 MPa) and also to a remarkable increase in the Weibull coefficient (the intervals of confidence of both values are overlapping only very slightly, see Figure 1). The difference between the Weibull plot for the uncoated glass and the TEOS-sol coated glass is large for low bending strengths and is decreasing monotonously with increasing bending strengths down to zero for maximum bending strength. This indicates that especially large—and therefore maybe more opened—micro flaws are healed by this coating by at least partial filling of micro flaws. Similar Weibull plots have been obtained for coated and uncoated 2 mm thick float glass plates. In this case it was proven by electron microscopy on samples, predamaged by Vickers indentation, that the TEOS sol is able to penetrate the micro cavity down to the bottom of the micro flaw and can fill it partially.[29]

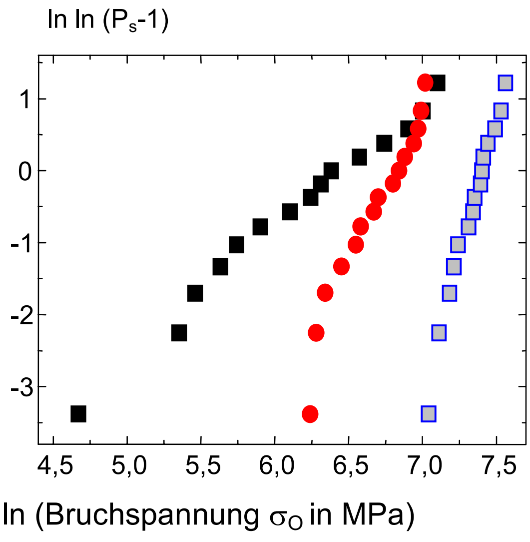

Fig. 1: Bending strength (double ring bending test with Weibull statistics) of uncoated (dark squares) thin glass (thickness 0.5 mm) and after coating with a thin (about 100 nm) SiO_2 layer (TEOS-sol) (circles) and an additional thick (2 µm) SiO_2 layer (bright squares) (MTKS-sol), both fired at 500°C.

uncoated:
s_0=434MPa, (410-460) MPa
m = 3.4 (2.1 – 3.9)
SiO_2 (TEOS):
s_0 = 749 MPa, (688-817) MPa
m = 5.9 (3.8 – 6.6)
SiO_2 (TEOS + MTKS):
s_0=1100 MPa, (1032-1146) MPa
m = 6.6 (3.9 – 7.1)

From Figure 1 one can also see that the combination of a TEOS coating with a 2 µm thick MTKS overcoat leads to very high bending strengths of about 1.1 GPa. The Weibull coefficient is also increased to about m = 6·6. That means that the 2-fold coating is improving the bending strength and also the reliability of the thin glass significantly. If one compares the Weibull plot of the TEOS coated and the TEOS+MTKS coated glass it becomes obvious that both plots are almost in parallel, e.g. the MTKS coatings increases the bending strength of the TEOS coated samples independent on their bending strength. This behaviour is different

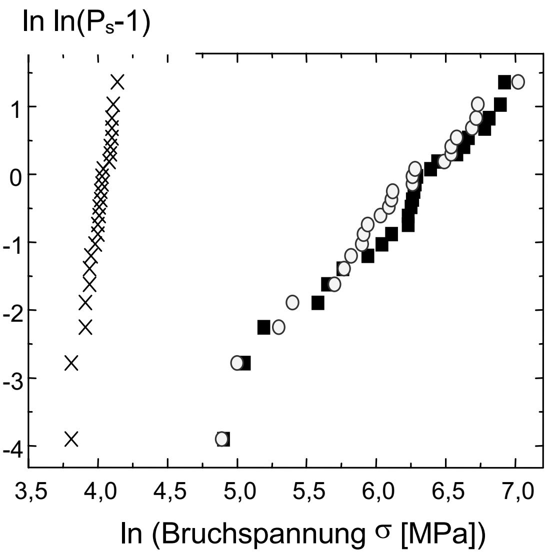

Fig. 2: Bending strength (double ring bending test) of float glass samples (10 cm × 10 cm × 2 cm) in the state of delivery (black squares), uncoated after sand falling test[28] and coated after sand falling test (coating synthesis see Ref. 26)
state of delivery:
s_0 = 628 MPa. (564-698) MPa
m = 3.4 (2.5-4.1)
x uncoated and sand trickled:
s_0 = 57 MPa. (56-58) MPa
m = 14.4 (10.9-17 8)
o coated and sand trickled:
s_0 = 571 MPa. (488-667) MPa
m = 2.3 (1.7-2.8)

from the uncoated and TEOS coated glasses. It was shown by electron microscopy that the 2 µm thick MTKS coating is covering micro flaw type of surface defects completely.[29] It is assumed that due to the high coating thickness and the very strong adhesion of the MTKS coating to the glass surface,[15] the bending strength increase is caused by a clamping effect of the MTKS-layer. The micro flaws, partially filled with the TEOS coating material are covered with the MTKS layer. This is in good agreement with results obtained earlier with 2 mm thick glass[29] and cutted glass rods.[16]

However, it is not possible that the TEOS + MTKS double layer can protect glass surfaces against mechanical attack.[29] Due to its very good chemical bonding and similar elastic modulus, defects generated in the coating will easily expand into the substrate.

This problem can be overcome by an organic-inorganic coating, which will be described in the next chapter.

Strength preserving coatings

Organic–inorganic coating (Nanomer®)

For these investigations, 2 mm thick float glass samples have been chosen as demonstrator samples for thin glass. The development of the synthesis route for the organic-inorganic protective coating is described elsewhere [26]. The strong protection effect of this coating is illustrated in Figure 2.

Figure 2 shows that the selected float glass samples have a very high bending strength of about 628 MPa in the state of delivery. This is much higher than usual values for float glass of about 120 MPa[29] and is attributed to a very careful handling and transportation of the samples directly from a float glass company. It can be excluded that tempered glass samples have been investigated, because the high strength drops down to 10 % by the sand falling test, which does not lead to any visible damage of the glass surface. Simultaneously, the Weibull coefficient increases significantly from 3.4 to 14·4 without any overlapping of the intervals of confidence (see Figure 2).

The Nanomer coating gives full protection against the mechanical attack of the sand falling test, as one can see form Figure 2. The intervals of confidence are overlapping very well for the bending strength and also for the Weibull coefficient. Similar protection effects can be obtained with organic polymer coatings.[17–23] However, here typical coating thicknesses are about 50 µm.[24] The thickness of the Nanomer coating is only 10 µm, which can be beneficial for display applications.

The Nanomer coating is damaged by the sand falling test, as one can see by light microscopy.[25] This means that the protection is obtained because the defects are not propagating and spreading down into the substrate under the given conditions due to imperfect chemical bonding between coating and substrate and different elastic behaviour. On the other side, the optical appearance of the coated glass is spoiled by the mechanical attack and this might be not suitable for display application. Therefore, it was interesting to investigate ceramic hard coatings, in order to improve the resistance of the glass surface against mechanical attack.

Ceramic coatings

For the investigation of ceramic hard coatings, a state-of-the-art ZrO_2 coating was deposited on a chemically toughenable special glass in order to obtain a comparison between the scratch hardness of the coated glass and chemically toughened glass (Na^+–K^+ ion exchange, performed by a glass processing company, experimental details are not available).

The scratch hardness was tested with a scratch tester (Rockwell diamond). After scratching (1 cm with 2 N load) the scratch depth was measured. The result is given in Figure 3.

One can see from Figure 3 that the scratch hardness

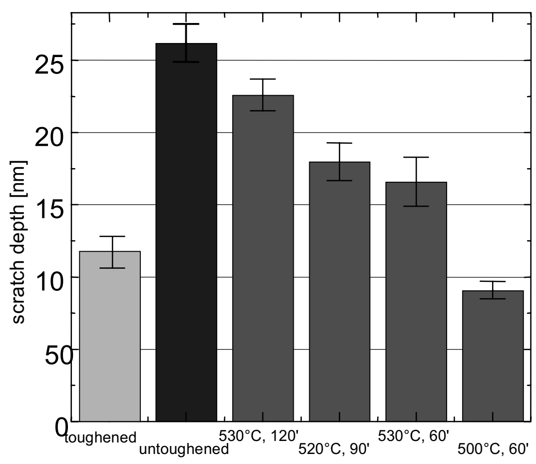

Fig. 3: Scratch depth after scratch test (1 cm with 2 N load, Rockwell diamond) in ZrO_2 coated and uncoated, chemically toughenable special glass, left bar shows the result for the toughened glass.

is increasing significantly by the chemical toughening process, because the scratch depth in the toughened glass (»100 nm) is much smaller than for the untoughened one (»250 nm). The dark grey bars in Figure 3 show the scratch depths which were obtained for ZrO_2 coated (thickness about 100 nm) glass for different firing conditions. After densification of the coating at 500°C for 1 h, a better scratch hardness is obtained than for chemical toughening. For higher temperatures, the scratch depth is much higher. This is surprising and cannot be explained at this moment. Further systematic investigations will be required for this.

It has to be mentioned that a scratch protection cannot be obtained by the ZrO_2 coating for a significantly higher load (10 N),[30] because the coatings are too thin and break like thin ice on water.

Optical coatings

Display glasses have to fulfil optical functions. One interesting feature is an antireflective coating based on well known interference layer systems for the reduction of the glare from surrounding light sources without affecting the clarity of the glass. Recently, coating sols with high (TiO_2) and low (SiO_2) refractive index, based on photopolymerizable nanoparticles have been developed[31] which allow the preparation of antireflective coatings on glass by dip coating or spin coating. Compared to state-of-the-art technologies (Schott Glaswerke)[32] the new coating sols allow to cure each single layer by 1 min of UV irradiation or thermal treatment at 120°C before the next one can be deposited. Finally, the whole coating stack of up to 7 single layers can be densified in one firing step (stackfiring).[31] The same coating systems are suitable to prepare NIR reflective coatings, which could be of interest for plasmadischarge panels where NIR radiation is induced that disturbs the remote control. By using the angle dependent dip-coating technique, efficient broad band NIR reflectors could be obtained with only 5 single layers.[33] The nanoparticles in these coatings from very smooth optical layers so that a very good scratch and abrasion hardness (2% haze after 1000 cycles of taber abrader test), UV and hydrolytic stability is obtained.[31]

Another optical function of a display glass can be the neutral colour absorption of visible light for contrast enhancement. Such coatings could be prepared with a combination of metal colloids (Ag, Pd) and metal ions (Co^{2+}) in a $PbO.SiO_2$ matrix.[34]

Conclusion

Most of the examples for functional coatings have been worked out with 2 mm thick float glass. A transfer of these results to thin glass seems plausible and should be possible without general problems. With this background, a high application potential for strength increasing and preserving coatings in combination with optical functions can be seen for display glasses. The appropriate production technologies will have to be developed in the future.

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