

Three different reasons for surface damages of glasses after machine dishwashing

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A variety of glass cups has been investigated after treatment in a machine dishwasher. Three types of surface damages were found.

The first type consists of clouding on the inner and outer surfaces appearing after about 1000 washing cycles. It can be related to the long range granular structure of glass, which is believed to be formed by thermal density fluctuation. During washing both water and detergents act as weak etchants, first eroding the smooth glass skin, then revealing the granular structure. As soon as the linkages between the granules are entirely broken by the etching, holes will manifest themselves at these sites. When the size of the holes (the hole width) reaches the half of the light wavelength, light scattering occurs and the glass seems cloudy.

The second type is the sheet clouding on the outer surface appearing after about 100 washing cycles. It can be related to holes on the surface, which are formed by the loss of the sphere domain phase from the SiO₂-rich matrix during washing. These domains result from phase separation induced by round-melting of the sharp cutting edge, which is responsible for local clouding of glass.

The third type is a golden film on the inner surface. These films are probably formed by complex formation between the glass surface and the organic compounds in the drinks.

All of the damages studied here are irreversible.

1. Introduction

Cleanness and shininess of the washed glasswares are most important to the consumers. Some problems after dishwashing, like spotting and food filming, can be solved by increasing temperature, adding rinsing aids, adding enough detergents, etc. If hard water filming (lime layer) occurs, it can be easily removed by soaking the glassware in an acid solution. Still, there remain some unclean and cloudy occurrences on the glass surfaces which are irreversible. A sound understanding of the underlying processes is important for prolonging the lifetime of glassware.

In the dishwasher the glass reacts with water and detergents at higher temperature and for much longer time than during handwashing. Recent studies indicated that the deterioration of glassware after repeated dishwashing is related to two types of corrosion behaviour [1 to 3]:

- a) uniform glass dissolution, which results merely in weight loss but does not affect the appearance of the glass;
- b) inhomogeneous degradation, that occurs only on the outer surface relating to compositional and structural inhomogeneities created by manufacturing processes.

The damages investigated already appeared after 100 washing cycles.

The work by Buchmeier [4] showed that the damages by clouding and iridescence were more serious when washing with a high disilicate-containing detergent (already after 50 cycles). The conventional and carbonate-containing compact detergents, however, did not cause visible corrosion even after 1000 washing cycles. But the disilicate detergent causes less glass weight loss than nondisilicate detergents. X-ray photoelectron spectroscopy (XPS) indicated that the disilicate built a coating layer on the glass surface with a structure similar to that of the basic substance. Additionally, the disilicate-containing detergent leached more ions from the glass than other detergents. In 1985, Gebhardt [5] published two types of damages after dishwashing: cord line and mouth rim clouding. She found that the cord line was elevated by washing and consisted of Al₂O₃ and ZrO₂, which were resistant to corrosion. The clouding ring on the rim originated from holes caused by inhomogeneous surface which created by evaporation products during round-melting the rim. Other works [6 to 8] paid more attention to the technical aspects and various factors were explored by studying the damage of glass surface, e.g. chemical composition, temperature, water pressure, water hardness, detergents, injured surface before washing, shapes of glass, etc.

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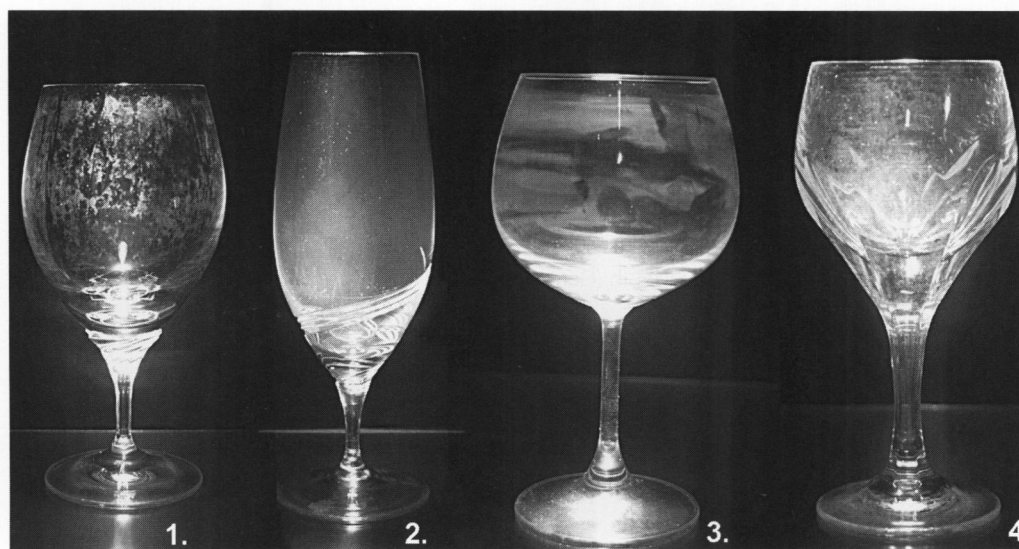


Figure 1. Four surface damaged wine glass cups after machine dishwashing. Cup 1: shows a continuous matt area and brilliant spots, cup 2: appears foggy all over, cup 3: displays sheet clouds on the outside, cup 4: has an additional golden layer on the inner surface.

Still, there are not many studies dealing with glass resistance to machine dishwashing. The origins of the damages involve the glass structure on different length scales (short range [9], medium range [10 to 15], and long range [16 to 18]), and relate to the water reaction and diffusion in glass [19], the phase separation of glass [20], and the reactivity of glass surface [21], etc.

Besides the visible damages many complex mechanisms should be investigated. Here, we will present a few of them in order to reveal deeper insight into the damage process occurring during dishwashing.

2. Experimental

The main task of this study is to explore the reasons for the damage of the glass cups presented in figure 1. Cup 1, 2 and 4 had been in use and had undergone machine dishwashing of an indefinite number of washing cycles. Cup 3 was a dishwashing test sample. After 100 washing cycles it turned cloudy and was taken out of the dishwasher. The other cups (without photos) served as assisting samples to understand the types of glass damages. They were final products of the glass industry and were stored in air without being used. One of them was taken as a reference sample (10 d in air). It was not treated any further and was investigated directly. The remaining cups underwent various washing cycles by machine dishwasher tests until visible damages appeared. One washed, yet undamaged cup was selected after 100 washing cycles as another reference sample. The inner, the outer and the fracture surfaces of the glasses were coated with carbon to avoid charging when being exposed to field emission scanning electron microscope (FE-SEM, LEO 1530, Carl Zeiss NTS Inc., Oberkochen (Germany)). All of the FE-SEM images were taken with an inlens detector at accelerating voltages between 0.8 and 2 kV to reveal the surface morphology of the samples. The chemical composition of the samples was analyzed with energy dispersive X-ray spectrometry (EDX, INCA 400, Oxford Instruments, Concord, MA (USA)) installed on the FE-SEM instrument. Some sample surfaces were examined by height mode atomic force microscopy (AFM, NanoScope Dimension 3100, Digital Instruments, Santa Barbara, CA (USA)).

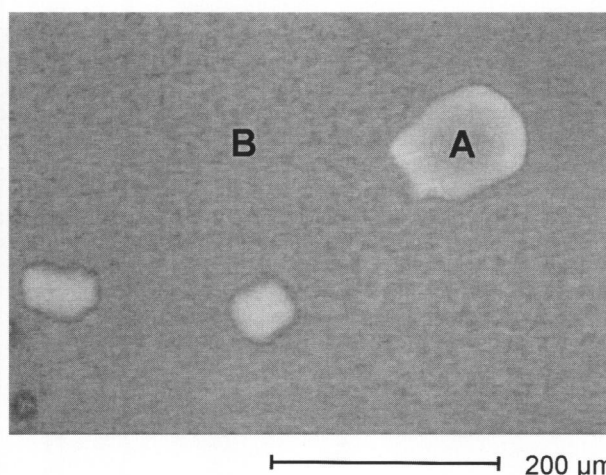


Figure 2. Optical microscope image of cup 1 of the outer surface showing the smooth brighter spots (A) and darker continuous matt area (B).

AFM allows quantification of the surface roughness. Element depth profiles of the samples were measured by using secondary neutral mass spectrometry (SNMS, INA 3, Leybold AG, Köln (Germany)).

3. Results and discussion

Figure 1 presents four glass cups damaged on the entire surface. Cup 1 shows a continuous matt area and brilliant spots. Cup 2 appears foggy all over. Cup 3 displays sheet wave clouding on the outside. Cup 4 has an additional golden layer on the inner surface. FE-SEM and AFM images were taken at different parts of the cups and revealed different damage patterns after dishwashing, which will be discussed individually.

3.1 Damages correlating to the glass structure

Figure 2 is an optical microscope image of the outer surface of cup 1. The smooth brighter spot (A) and the darker con-

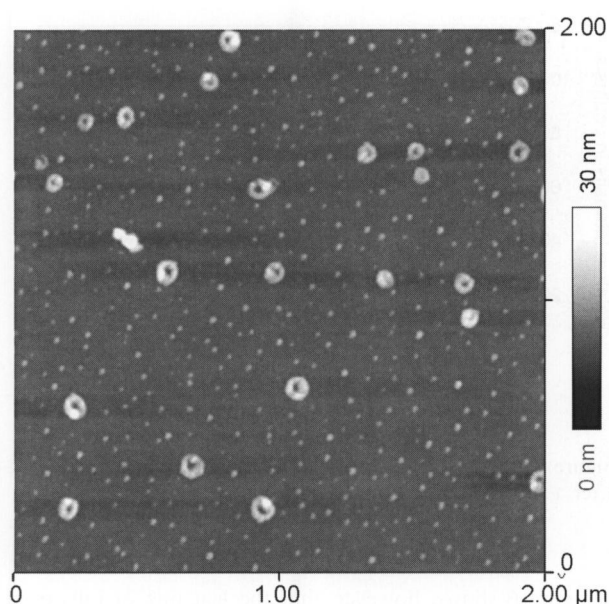


Figure 3. AFM image on the inside of a virgin wine cup (no photo) exposed to air for 10 d, showing the corrosion droplets.

tinuous matt area (B) were examined further by AFM. The height mode AFM image on the brighter spot (A) reveals droplet traces after dishwashing. This area is relatively smooth with a lower root mean square (rms) roughness value of 0.83 nm measured on a $(5 \times 5) \mu\text{m}^2$ image, in spite of the large undulation on the surface. The AFM image of the continuous area (B) shows a granular structure. This area is rougher than spot (A) with a higher rms roughness value of 1.4 nm ($(5 \times 5) \mu\text{m}^2$ image). The two different areas are clearly different in their features.

To realize what happens after washing, it is necessary to study the virgin glass surface. Figure 3 shows an AFM image of the inside of a wine cup (no photo) exposed to air for 10 d. The cups were produced by blowing a piece of molten glass into a mould. Then the blow-cap was cut off and the sharp edge was remolten. The inside of the cup usually lacks any defects functioning as an ideal of the surface helping to explore the nature of glass. Figure 3 reveals that there are minor droplets on the glass surface in addition to the larger visible droplets. It was observed also that washed off droplets leave etched traces on the glass surface. Such corrosion droplets and their etching behaviour on glass skin were studied previously [22 and 23]. The AFM investigation on the washed atmosphere side of float glass [23] revealed the same pattern as observed by us. It can be concluded that the brighter spot (A) on cup 1 is the original glass surface whereas the matt area (B) with the granular pattern reveals the inner structure of the glass after the glass skin had been eroded. The granular pattern has also been observed on many other glass fracture surfaces [16 and 17]. Hence the results obtained from cup 1 indicate the existence of a glass skin as proposed earlier [22]. The glass skin can protect the glass against attacks from the corrosive media and can also result in inhomogeneous corrosion appearance if previously injured [22 and 23]. During production the outer surface of the wine cup contacts the metal mould. The process comes along with inhomogeneous stress and temperature distributions on the glass surface, which probably results in inhomogeneous migration of the ions onto

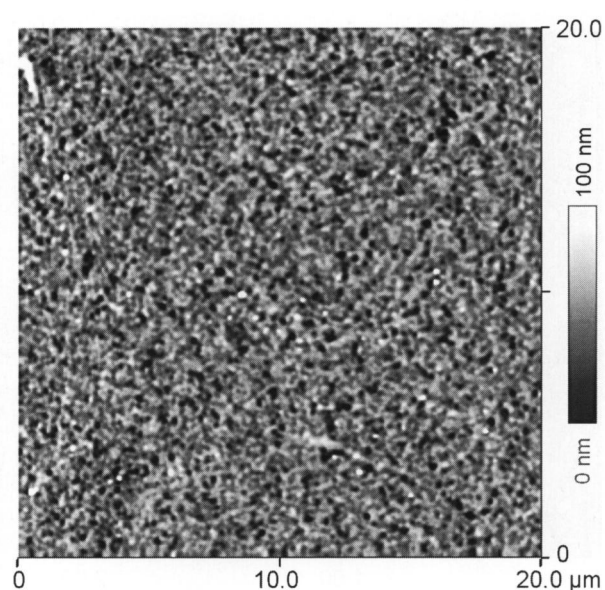


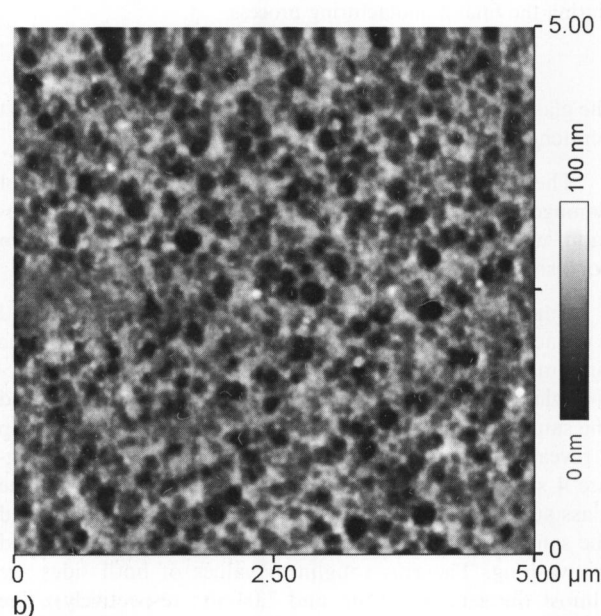
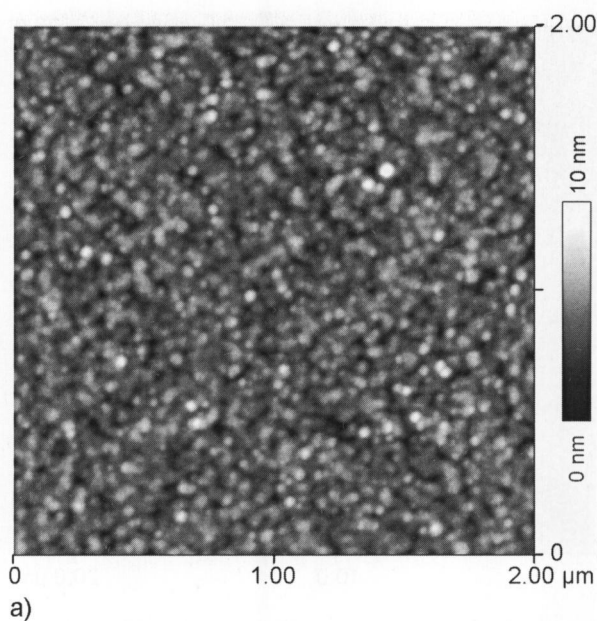
Figure 4. AFM image of the inside of cup 2 polished with acid during the final manufacturing process.

the glass surface [4]. Moreover, during storage and transport scratches and dirtying could spoil the surface.

Therefore the corrosion behaviour heavily differs. Spot damage patterns on the outer glass surfaces are most common, while the inner surfaces usually show rather uniform corrosion features after repeated dishwashing.

Cup 2 looks as if uniformly corroded. It was polished with acid to remove unevenness on the surface during the final manufacturing process remarkably eroding the protective glass skin. The exposed surface should be structured the same as in bulk. The AFM studies on both sides of cup 2 revealed the same porous features, see for example in figure 4 showing the inside of cup 2. This indicates that the glass surfaces on the inside and on the outside both faced the same primordial conditions and were equally corroded by washing. The rms roughness values of both sides are almost the same (7.21 nm and 7.04 nm, respectively). The porous structure in figure 4 consists of holes of about $1 \mu\text{m}$ in size. Those holes are responsible for the presence of the foggy appearance of cup 2. At higher magnification the constructive units of the surface revealed by AFM are detected as granules of 20 to 30 nm in diameter (not shown here).

In order to obtain a general evolutionary concept on glass corrosion in the case of dishwashing, numerous glasswares (no photos) were examined by AFM of the inner surface at different washing stages. After 100 washing cycles the glass is still transparent and shining, but the AFM image (figure 5a) reveals a homogeneous granular structure and the surface already lacks its protective glass skin. The higher resolution AFM image (not shown here) indicates that the granules are sized 20 to 30 nm. In spite of the homogenous feature of this sample, the roughness value is 1.45 nm, i. e. larger than that of glass skin. With increased number of washing cycles the release of group of granules from the glass is induced. After 1000 washing cycles the glassware is visibly cloudy. The AFM image in figure 5b shows a honeycomb pattern. The roughness value abruptly increases up to 11.70 nm. Holes of about 600 nm in size scatter the light,



Figures 5a and b. AFM images of the inner surfaces of various wine cups (no photos) at different washing stages; a) at the earlier stage after 100 cycles, the glass looks still transparent, and b) at the damaged final stage after 1000 cycles, the glass appears cloudy.

also mentioned in [4]. It needs to be noticed that the two AFM images are presented on two different height scales (10 and 100 nm). If they are treated on the same height scales, figure 5a shows a rather flat surface, figure 5b shows a rather rough one with holes of various sizes resembling a honeycomb.

For the very first time we found that the glass is not eroded uniformly as described in [2], but dissolved in pieces during dishwashing, which results both in morphological changes and weight loss. Therefore the clouding mechanisms of glassware need to be reconsidered. Leaching of ions and dissolving of glass network are commonly accepted to be the main clouding process. The SNMS investigation

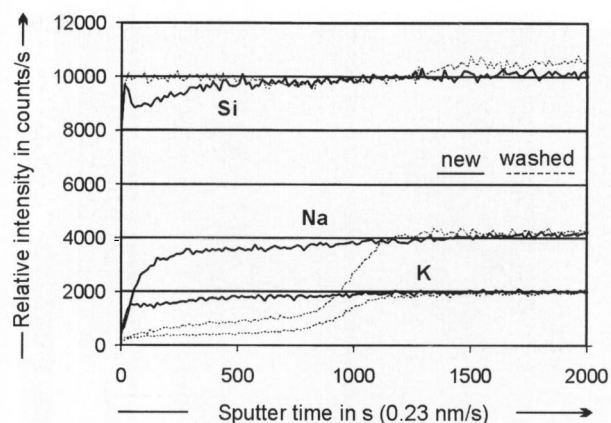


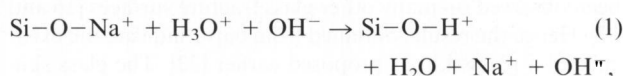
Figure 6. SNMS depth profiles of a new cup surface and of one after a short washing time (100 cycles).

in figure 6 shows, however, that the leaching of ions does not directly relate to the cloudy appearance. After a short washing time (100 cycles) Na^+ and K^+ ions had heavily been leached out and had left a 200 nm ion-poor near surface region. Meanwhile the silicon concentration remained almost unchanged before and after washing. We observed that the glass is still far from visible clouding after 100 washing cycles. In other words ion leaching plays only a minor role in this process. As soon as the cross linkages around the granules have been broken, the glass could turn cloudy. The notion of density fluctuations in the liquid glass would best explain our observations concluding that glass is composed of both higher density granules and lower density linkages. A detailed discussion of such a long range granular structure is beyond the scope of this paper and will be published later.

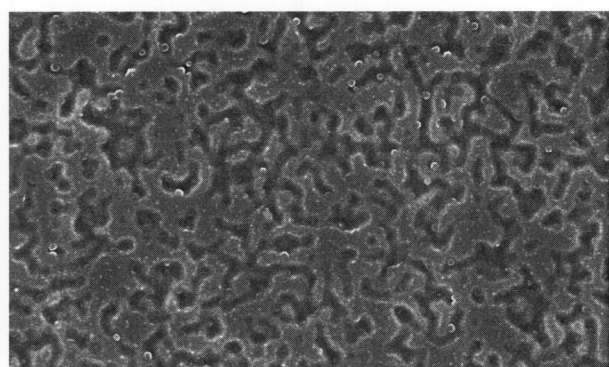
The corrosion line of glass via dishwashing may be summarized as follows:

- erosion of the covered glass skin,
- exposure of the granules,
- breaking of the linkages around the granules,
- loss of groups of granules,
- formation of holes.

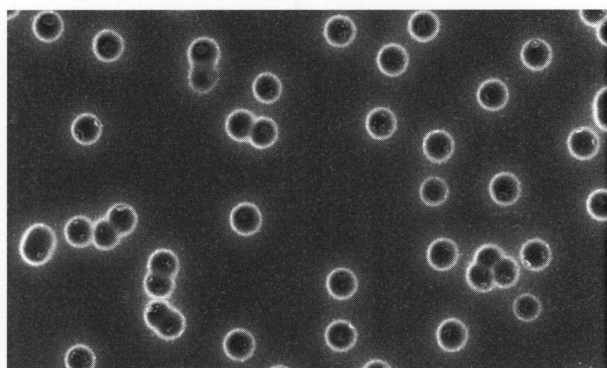
We now turn to the differences in the corrosion behaviour of glasses under ambient conditions and in the dishwasher. Many corrosion studies confirmed that there is mostly gelation and leaching of alkali ions in the acid to neutral pH ranges. In the alkaline pH ranges the glass network is dissolved [4]. Due to the existence of hydrophilic ions in glass water droplets are formed on the glass surface. Within the droplets ions are replaced by water (or H_3O^+) and subsequently the local pH value increases. At $\text{pH} > 9$, the network is broken [25].



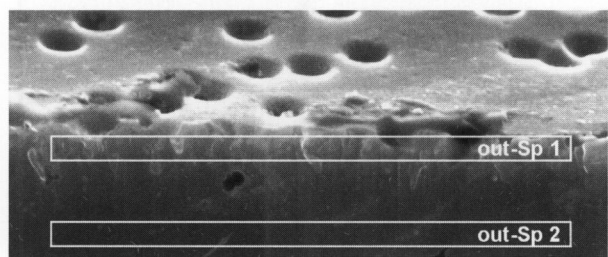
Here the water is static, which enables the increase of the pH value during the ion exchange. Yet, with the dishwasher the leached ions are removed immediately by the exchange



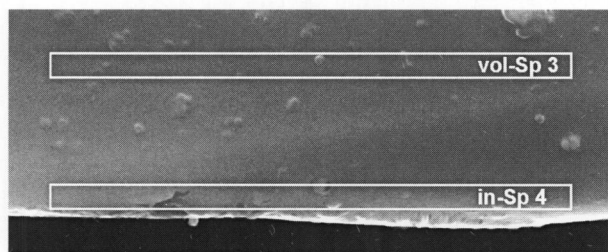
a) 4 μm



b) 4 μm



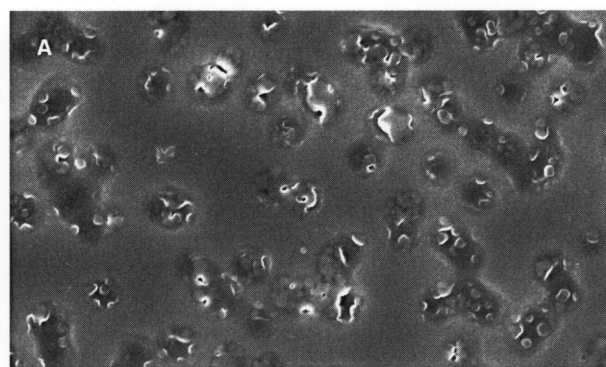
c) 1 μm



d) 1 μm

Figures 7a to d. FE-SEM images of cup 3; a) on the surface area showing bi-continuous phase separation pattern, b) on the surface area showing isolated sphere phase separation pattern, c) on the fracture near the outer surface, d) on the fracture near the inner surface. The frames inserted in 7c and d indicate the EDX analysing areas.

of the water. The main process of corrosion in dishwasher should hence be explained by the reaction between water and glass network. The recent study [19] of diffusion of water into silica glass enlightens this reaction. The infrared spectra display two main absorbance peaks in the measured



1 μm

Figure 8. FE-SEM images of cup 3; enlarged image of the fingerprints on a contacting line.

range of a water vapour treated silica glass. The peak at 3670 cm^{-1} is attributed to hydroxyl ($-\text{OH}$) and the peak at 3425 cm^{-1} to molecular water (H_2O). Water in silica glass reacts with the glass network by



This means that water alone can break the glass network but at a very slow rate if the reaction is at lower temperature range than in a dishwasher. But if the network bonds were under strain (length and angle), the water molecules could break the bonds easily. The water molecules very likely diffuse prior to the interspace of the granules and the reaction in (3) preferably takes place there. As soon as the lower density linkages are broken, the granules will release from the bulk. As a result, holes develop and finally cause light scattering. This is the primary reason for the clouding of glass. Reinforcing of the weak linkages could thus prolong the lifetime of the glass. A zinc-containing stone hung in a dishwasher will postpone the clouding process, probably because zinc has a high coordination number and can connect the broken network in the lower density areas. Therefore the elements with high coordination state, such as Co, Ni etc., can be used to prolong the lifetime of glasses [26].

The study in [4] indicated that disilicate-containing detergent can cause clouding earlier, however not by leaching out more ions but by producing a coating layer on the glass surface. This possibly holds only for certain granules whereby the roughness of the surface is enlarged finally leading to the scattering of light.

3.2 Damage correlating to the production process

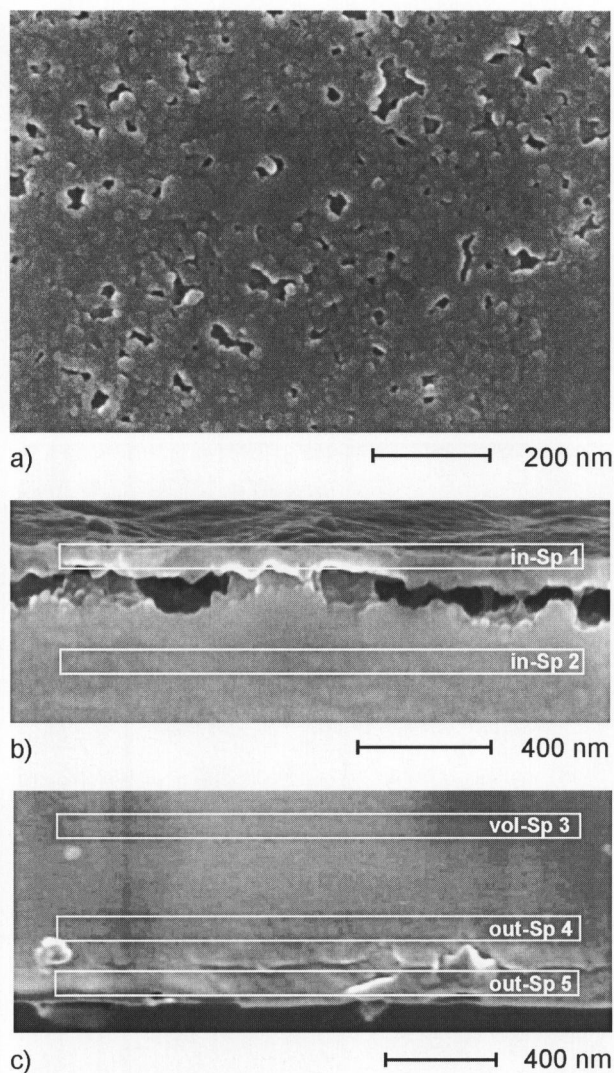
Cup 3 was examined in various regions. It was ascertained that the inside and the bottom of the outside do not bear any damage at all whereas major parts of the outside reveal various damage patterns depending on the specific zone. Figures 7a and b are examples showing a bi-continuous domain pattern (figure 7a) and an isolated sphere domain pattern (figure 7b). The measurements on the fracture confirmed that the patterns were formed by a dissolved phase and a continuous matrix phase as shown in figure 7c. The inside remained unaffected (figure 7d). AFM images of the outer surface confirm further that the dissolved phase ap-

Table 1. Elements in atom% detected by EDX on the fracture surface of the cup 3 at 10 kV scanned for 100 s

	O	Na	Si	K	Pb
out-Sp 1	74.05	1.99	21.38	1.24	1.34
out-Sp 2	63.92	3.74	26.55	3.60	2.19
vol-Sp 3	59.22	4.55	28.52	5.10	2.81
in-Sp 4	53.12	3.70	33.97	5.66	3.55

pears as grooves and holes on the surface (not shown here). The EDX analysis indicates that the lost phase is the Pb-rich phase since Pb is much rarer around the damaged outer surface (out-Sp 1; table 1) than elsewhere. The flame treatment to round-melt the sharp edge might very well sign responsible for this effect as was the case in our previous studies [1]. The spreading of the flame all over the entire surface is probably due to the specific round shape of the glass since the same damaged pattern was observed on glass with the same shape like cup 3 as reported in literature [4]. The contour of the glass may lead the flame (600 to 2000 °C) to flow towards the bottom instead of being limited to the rim. The glass surface is obviously exposed to different temperature regimes when in contact with the flame. Subsequently, different phase separation patterns are established. However, not every single round cup is affected, there are certainly other deviations contributing during the production process at the rounding stage, such as wind, vibration, etc. This sort of damage merely occurred occasionally, yet is observed much earlier (already after 100 cycles) than with cup 1 and cup 2. These defects are due to manufacturing. Washing only makes them visible. Initially the phase separated surface was covered by a denser SiO₂ skin [23]. The refractive indexes of the Pb-rich phase and the SiO₂-rich matrix remained insignificant and would not cause light scattering. After the glass skin had been eroded, the Pb-rich phase was dissolved. The surface would scatter light as soon as the size of the dissolved phase exceeded the half of the light wavelength. In order to ascertain the real features of the cloudy area AFM and FE-SEM measurements were carried out on the surface as well as on the fracture surface. When the cloudy glass was studied only with SEM, it became difficult to distinguish the elevated from the depressed parts [2]. Phase separation remained too insignificant a phenomenon as to enable any definite conclusions.

Further useful pieces of information were obtained on cup 3. There were fingerprints on the glass surface. They became visible only after the cloudy damage appeared. They could not be removed by acetone or any other fat-soluble organic substances. The FE-SEM and AFM investigations showed that the lines of the hand impressed on the glass consist of thin layers covering the Pb-rich domains (figure 8). The EDX analysis indicates that there is an additional NaCl composition there. The NaCl salt possibly reacts or mix-crystallizes with the SiO₂-rich glass skin, thus prolonging the lifetime of the skin. After the neighbouring Pb-rich phase had been dissolved the fingerprints on the glass manifested themselves. It is a coincidental result which offers a method to increase the resistance of glass to corrosion. Recently, it was demonstrated [27] that if a new glass surface was treated with AlCl₃ salt the lifetime could be prolonged. This may follow the same mechanisms as as-



Figures 9a to c. FE-SEM images of cup 4; a) inner surface, b) fracture near the inner surface, c) fracture near the outer surface. The frames inserted in figures b and c indicate the EDX analysing areas.

sumed here, which means that enhancing the glass skin is another very useful method for improving dishwashing resistance of glasses.

3.3 Damage by forming organic complexes from drinks on the inner glass surface

Cup 4 shows a golden film on the inner surface. In most cases the additional golden hard layer was built by lime from hard water. It consists mainly of CaCO₃ and can be removed by acetic acid or citric acid. A piece of cup 4 was accordingly treated and cleaned with an ultrasonic bath at 60 °C for 1 h. The golden film, however, remained. AFM examinations helped to characterize the cup. They revealed granular patterns (rms roughness = 1.4 nm) and honeycomb patterns (rms roughness = 12.2 nm) on the outside as well as flock pieces (rms roughness = 21.5 nm) on the inside. Thus it follows that the outside is still glass surface and the inside is covered with a layer. In order to understand the damage better FE-SEM investigation was carried out on the inner

Table 2. Elements in atom% detected by EDX on the fracture surface of the cup 4 at 20 kV scanned for 300 s

	C	O	F	Na	Al	Si	K	Ca	Ba	Pb
in-Sp 1	48.08	43.46	1.32	0.40	0.05	5.53	0.62	0.08	0.04	0.49
in-Sp 2	20.79	60.10		0.99	0.07	14.11	2.39	0.07	0.14	0.49
vol-Sp 3	10.52	59.33		1.08		21.92	4.74		0.25	2.16
out-Sp 4	12.57	61.19		0.84	0.26	20.23	2.81		0.21	1.89
out-Sp 5	15.45	54.53		0.79	0.64	23.50	3.12			1.97

surface as well as the fracture surface of cup 4. The FE-SEM images show that the golden film covers the entire inner surface but is not watertight (figure 9a). When viewed on the fracture the additional film was seen more clearly. It is about 80 nm thick and the glass underneath is heavily corroded (figure 9b). The other side shows a lower density band of about 150 to 200 nm in width (figure 9c), which is typical of water corrosion [25]. The EDX values are given in table 2. Since the electron beam is larger than the analyzed area the results can only be considered as semi-quantitative. There is more carbon on the golden film than elsewhere on the cup, whereas there is less silica. Additionally, the calcium in the film is insignificant, so a lime film could not be formed. Note the film is merely on the inside. Conclusively, the golden film might be formed by the reaction of organic substances in drinks with the glass surface [26]. If the complex building is used as a protecting coating layer against the attack of water, it must be considered whether the layer is tight or not. In the case of cup 4 the layer is not watertight and can not block water corrosion. On the contrary the inside was corroded much more severely than the uncoated outside. The analysis therefore recommends avoiding useless or contra productive coating processes.

4. Conclusion

Surface damage of glasswares after dishwashing can be induced by a number causes. We have demonstrated that there are three types of damage to be classified. The first is related to the very nature of the glass. Water acts as weak etchant preferring lower density areas. The investigations made density fluctuation structure of glass visible. Enhancing the linkages by adding elements of high coordination state could remarkably prolong the lifetime of glass. The second type of damage is related to phase separation caused by the heating during the final round-melting process. Different temperature regimes cause different damage patterns, which can be revealed by the corrosion process. The accidental detection of the fingerprints leads to the assumption that treating the glass skin with NaCl could keep glasses shiny much longer. The third damage related to the complex-building of organic compounds with the glass surface shows that corrosion might even be furthered underneath the layer because it promoted bad water exchange leading to the local increase of the pH value. Additional research is, however, indispensable.

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