Original Paper

Local clouding of glass after machine dishwashing

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The local clouding of glasses after dishwashing near the mouth rims on a coffee pot made from borosilicate glass, on a wine cup made from lead crystal glass and near the stem base on a wine cup made from barium silicate glass has been found to be due to damage during manufacture. The examined clouding is different from the two well known types of filming and etching cloudiness related to the reactions of glass with water and detergent in the dishwasher. The intensive study on the wine cup of lead crystal glass shows that a phase separation was induced during the flame treatment on the sharp rim and base. The aggregates of Pb-rich spheres scaled off when the thin covering of SiO_2-rich skin was eroded away and consequently holes were formed on the glass surface on the micrometre scale, which resulted in light scattering and the clouding of the glassware. Evaporation species from warmer regions onto the colder areas of the glass surface could be observed, but they are not the reason for the local clouding in this study. Dendritic thin corrosion products caused by air exposure could be detected on the undisturbed glass surface as well.

1. Introduction

After certain washing cycles with a machine dishwasher some glassware may appear cloudy. The cloudy appearances can occur in the form of spots, sheet clouds, yellow films, particles, bands etc. and may be scattered over the whole surface, or appear in localized areas e.g. near the mouth rims and stem bases of glasses. It is crucial to identify the type of cloudiness in order to determine the ultimate cause of these glass defects and to find ways to deal with them. Two typical types of cloudiness have been mentioned in the literature: hard water filming and etching. Some researchers have intensively studied these two glass damages induced by various dishwashing detergents, at different washing temperatures and with different water hardness [1 to 4]. These damages stem from the distinct nature of glass and its interaction with water and detergent. However there is another, completely different damage related to production defects. It may occasionally play a more important role, because this type of cloudiness occurs much earlier than the former with the glassware losing its value for the consumer. Although several studies [4 and 5] have been performed on these phenomena, they have not been well understood due to the limitations of the experimental methods available at the time. As early as in 1974, Lohmeyer [4] pointed out that localized differences in chemical composition due to melting-off and annealing produce local differences in resistance to attack by various media. The research work was carried out with optical microscopy, making it impossible to pin-

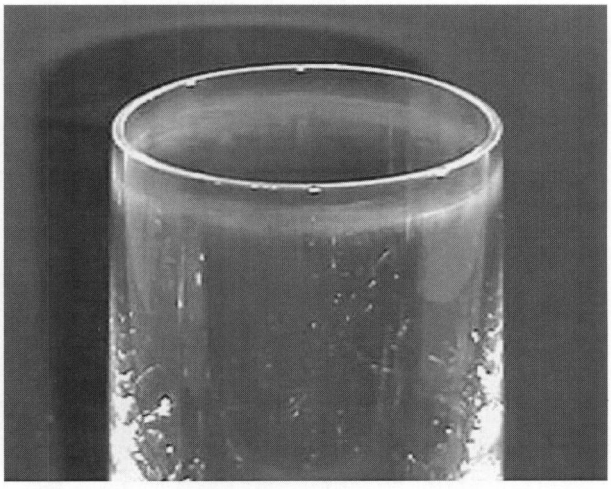

Figure 1. Local clouding near the mouth rim of a barium silicate drinking glass.

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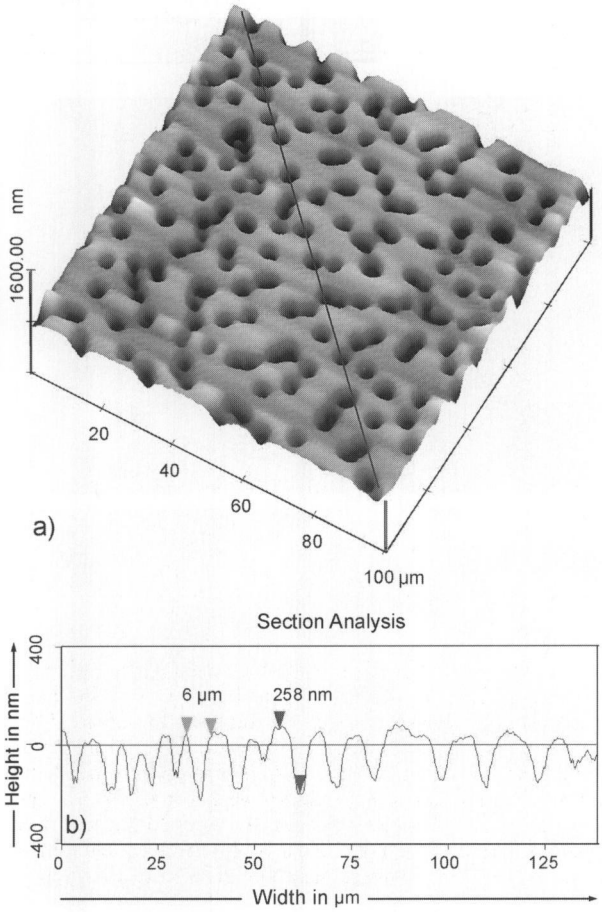
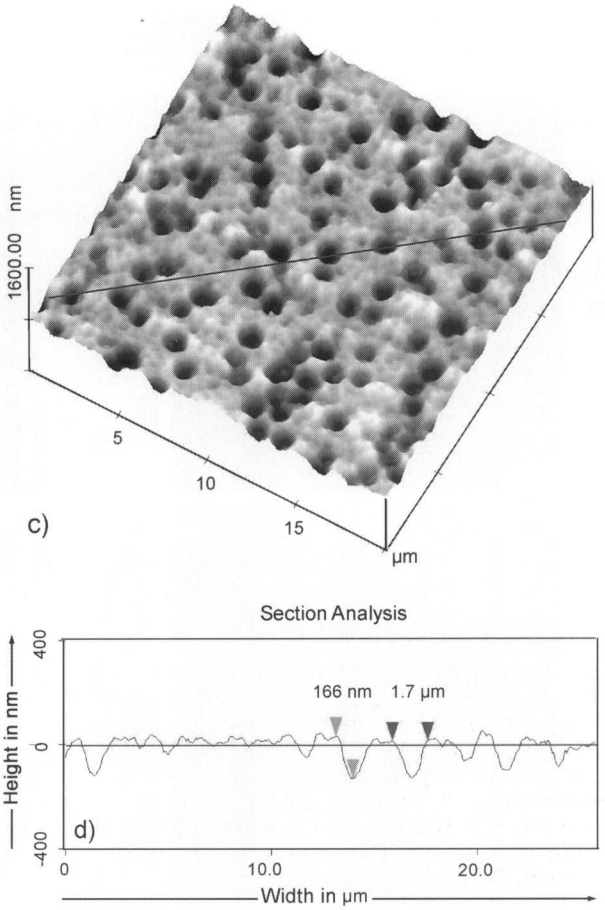
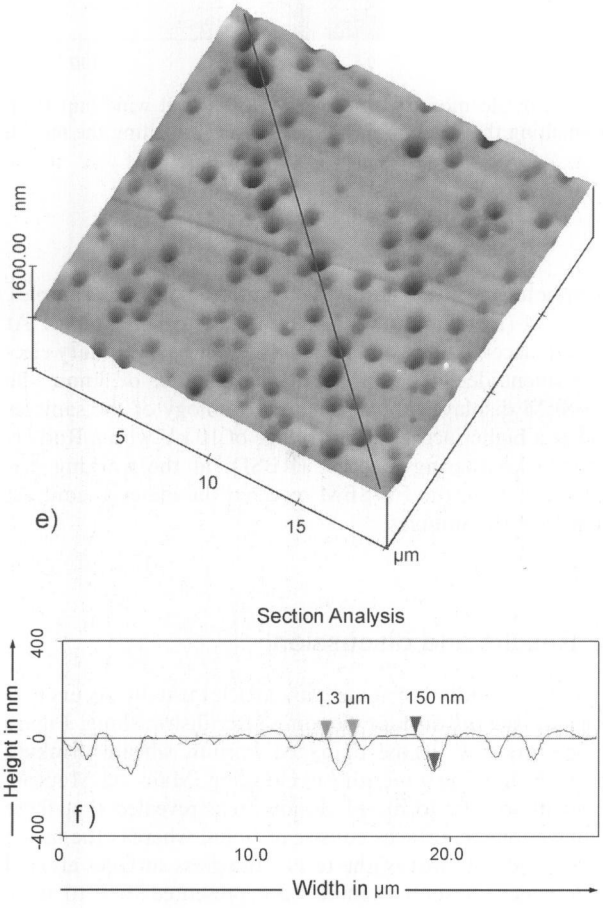






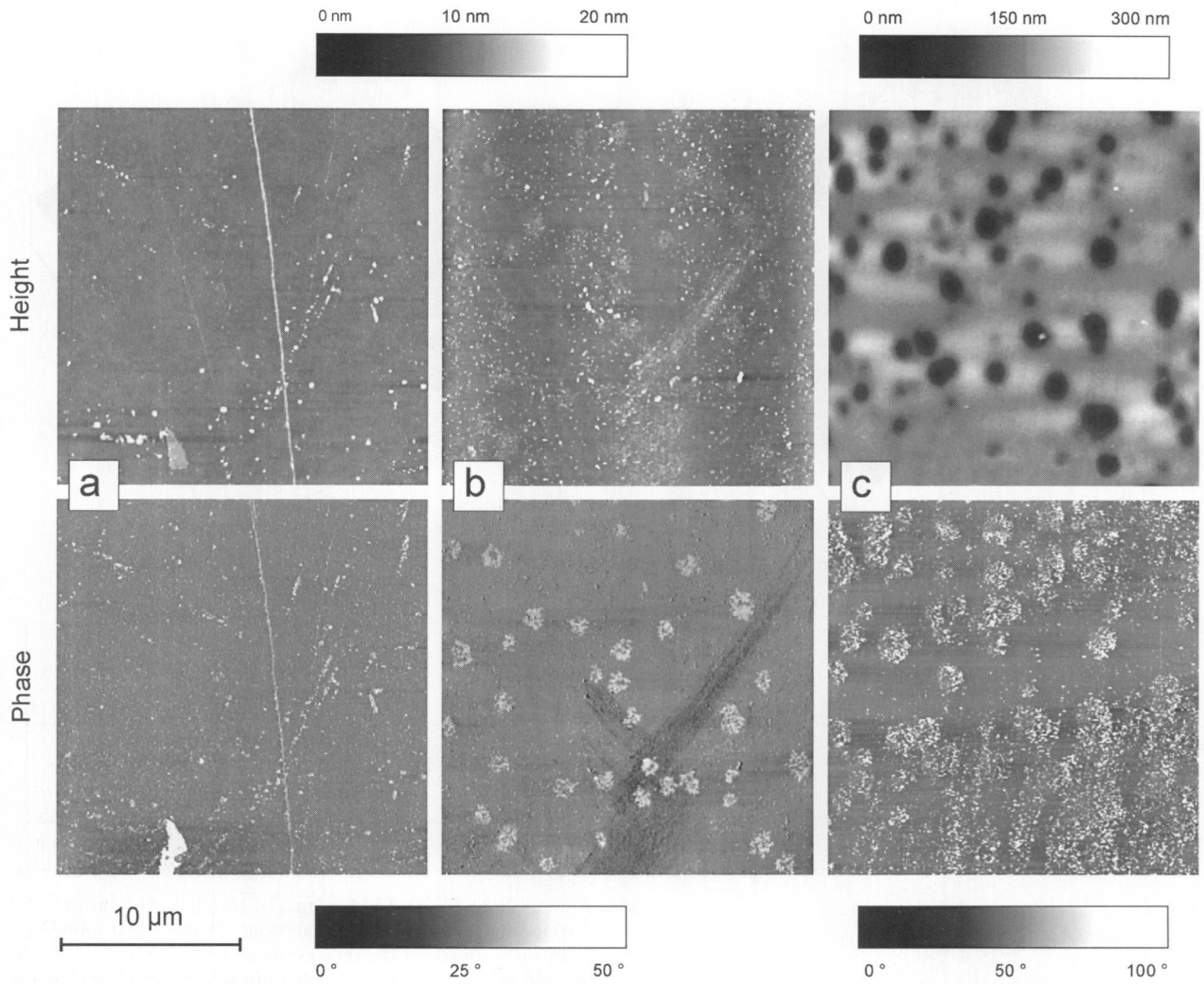
Figures 2a to f. 3-D AFM images of cloudy areas and the corresponding analysis of cross sections as measured along the solid lines shown in the images; a) and b) cloudy ring on the bottom of the stem base of a barium silicate wine cup, c) and d) cloudy band ring near the mouth rim of a borosilicate glass coffee pot, e) and f) cloudy ring near the mouth rim of a lead crystal glass wine cup.

point the exact origin. Then, in 1985 Gebhardt [5] published a paper on dishwasher resistance of glass investigated by scanning electron microscopy and infrared reflection spectroscopy which put the research much further than ever before. She pointed out that the mouth rim clouding of a drinking glass could be due to the formation of holes in this area. The infrared spectroscopy showed that after round-melting the mouth rim, an enrichment of the alkali ions took place, which according to Gebhardt was responsible for the clouding after dishwashing. However, the experimental methods employed are not sufficient to fully justify her proposal. With the rapid development of modern characterization methods in recent years such as field emission scanning electron microscopy (FE-SEM) and atomic force microscopy (AFM) many phenomena can be clarified much better. In this paper, the origins of the local clouding on mouth rims and stem bases are studied by FE-SEM and AFM in more detail.

2. Experimental

2.1 Samples

Wine cups are produced by blowing a piece of molten glass in a mould, after that the blow-cap is cut off. In order to



Figures 3a to c. AFM images in height and phase mode of the areas near the mouth rims of the lead crystal wine cup from subsequent processing steps, a) after cutting the blow-cap and before re-melting the sharp mouth rim, b) after re-melting the mouth rim, c) after dishwashing for many cycles.

round the sharp cutting edge, a flame is used as the cheapest and most convenient technique. Three lead crystal wine cups obtained from successive producing steps on the assembly line were investigated near the mouth rims. The examination was carried out on the samples after cutting, re-melting and dishwashing (clouding). Additionally, the wine cup taken from the re-melting stage was intensively studied on the whole surface.

The defect borosilicate coffee pot exhibited a cloudy band about 4 mm in width near the rim area, whereas the barium silicate wine cup showed a ring-shaped clouding on the bottom of the stem base. The two glass products were in use for an indefinite period of time. Except for the cloudy band region, most of the glass surfaces still prevailed their brilliance and transparency.

2.2 Analysis

AFM (Digital Instruments NanoScope Dimension 3100) in height and phase mode was used to image the surface morphology and material distribution of some samples. FE-SEM (LEO 1530) was used for some other samples. At a lower accelerating voltage of 0.8 kV with a secondary electron Inlens detector at the working distance of 3 mm, the FE-SEM displayed the surface morphology of the samples and at a higher accelerating voltage of 10 kV with a Rutherford backscattering detector (RBSD) at the working distance of 9 mm, the FE-SEM revealed the material contrast images of the samples.

3. Results and discussion

The local clouding of some glass articles usually occurs earlier than the full surface clouding after dishwashing. Figure 1 presents one of the damaged barium silicate drinking glasses exhibiting a mouth rim clouding. Many AFM measurements on the localized cloudy areas revealed that these damaged glass surfaces consist of holes, whereas the inside and outside of most of the rest of the glass surfaces are still undamaged. Several examples are presented here to illus-

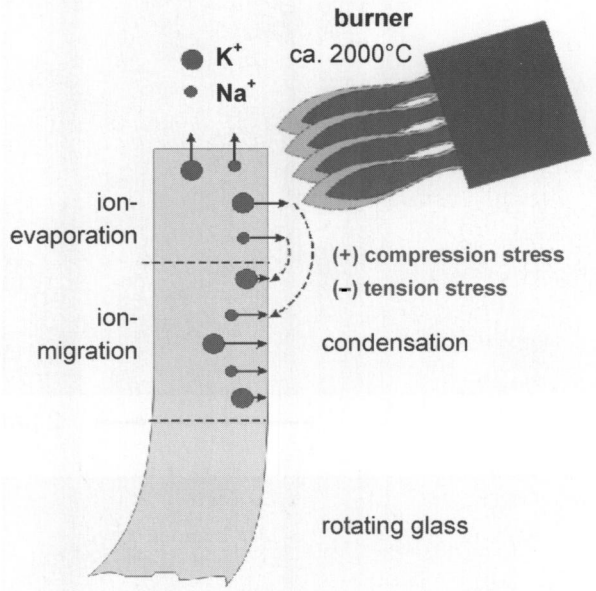
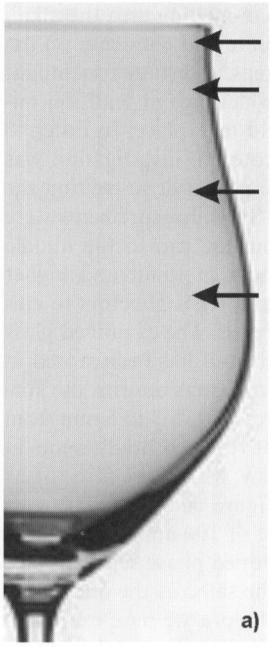
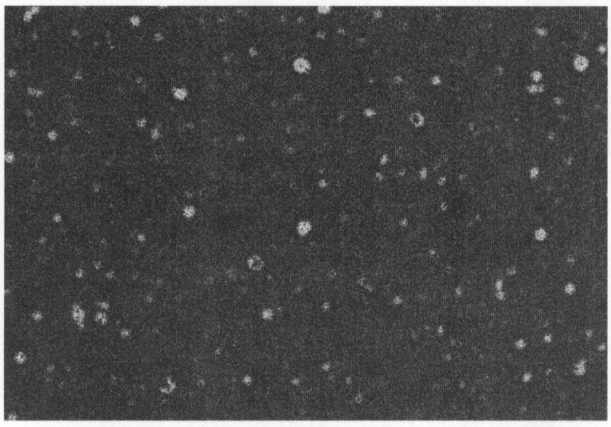


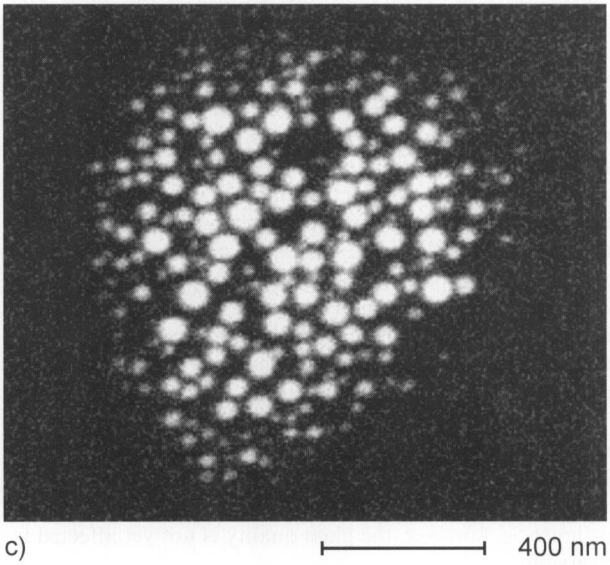
Figure 4. Scheme of the re-melting of the rim.

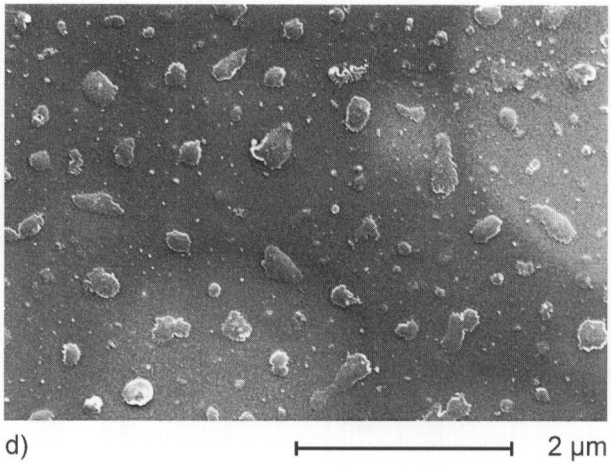
trate this phenomenon. Figure 2a shows the 3D-AFM image of a cloudy ring on the bottom of the stem base of a barium silicate glass. The section analysis along the solid line in the image (figure 2a) indicates that the holes measure about 6 µm in diameter and about 250 nm in depth (illustrated in figure 2b). Another example of the local clouding was taken on a borosilicate coffee pot (figures 2c and d). The featured cloudy ring on the sample is located at a position of 3 mm from the re-melting rim on the outside and measures about 4 mm in width. As illustrated by figures 2c and d, the holes are about 1.7 µm wide and their depth is about 160 nm. Figures 2e and f show the local clouding area of a lead crystal wine cup near the mouth rim with holes of about 1.3 µm in diameter and 150 nm in depth. The clouding on the examined glasses is due to light scattering. To understand the formation of the holes, the AFM investigations were intensively carried out on glasses taken from different processing steps by choosing the easier available lead crystal glass articles.

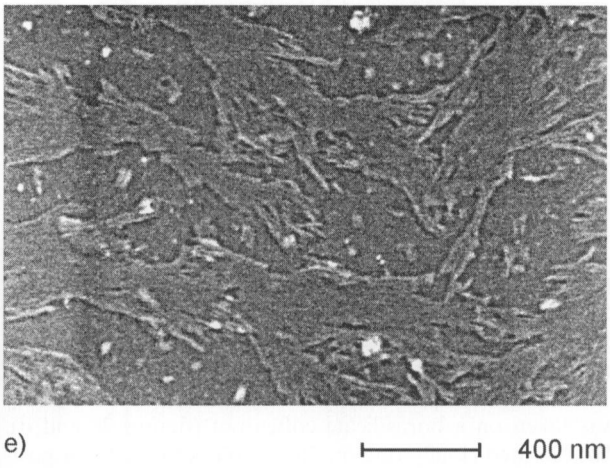
An intermediate product of a wine cup after cutting and before re-melting, a fresh final product after re-melting before washing and a damaged product which has a cloudy ring near the mouth rim after many cycles of washing were investigated in the areas near the mouth rims. Figures 3a to c show the series of AFM images in height and phase mode. Before re-melting, only accidental scratching and dirt pieces are observed. The height and phase images show no differences as presented in figures 3a. After re-melting, before dishwashing the height image of the sample is almost featureless, but the phase image shows clear bright spots in a size of about 1 µm as shown in figure 3b. After certain cycles in the dishwasher, the wine cup has a cloudy ring with a width of about 2 mm at a distance of 3 to 4 mm from the re-molten rim. This area turns out to consist of holes with a diameter of about 1 µm and a depth of about 150 nm as shown in figure 3c. It is reasonable to suppose that a phase separation occurred during the re-melting process and the isolated phase (spheres) was preferentially dissolved or scaled off in the detergent. Figure 4 is the schematic drawing of the burner and the glass. In the re-melting area the alkali and earth alkali ions might evaporate and condense on the colder area. Between these two areas, a certain zone might be long enough at temperatures which favour lead ion migration and phase separation could take place. In order to obtain information in detail, a thorough investigation was carried out on a lead crystal wine cup after re-melting the rim without dishwashing. The FE-SEM measurements were done along the wine cup wall from the rim to the middle position as shown in figures 5a to e at lower and higher accelerating voltages with Inlens and RBS detectors to collect various messages at different levels. The examined glass has the form presented in figure 5a and has been stored in air over one year. Within 2 mm area from the rim the surface is very flat without any feature. Within 3 to 5 mm from the rim the FE-SEM measurement revealed bright spots at higher accelerating voltage of 10 kV with RBS detector as presented in figure 5b, which in figure 5c are shown to be aggregates of spheres with the size of 100 nm. This is clear evidence for an incompletely developed phase separation of the sample. This phenomenon is the same as the one in our previous research work [6]. In that work we have examined the surface change of a fire-polished lead crystal bowl. It was found that the after-treatment with flame induced strong enrichment of lead on the bowl surface with a black colour. A monolayer of spheres spread on the whole surface just beneath an SiO_2 glass skin. It might have been induced by the reduction of Pb^{2+} to Pb^0 in reducing flame gas. Finally, a lead-rich sphere phase was formed in the SiO_2-rich glass matrix. With the subsequent acid polishing this sphere layer can be removed easily as well as the pressing burrs and cold waves. Acid polishing can also be used to remove the layer of the spherical aggregates on the wine cup to avoid the formation of holes after dishwashing and to increase resistance to local cloudy damage as mentioned in the literature [5]. When the voltage was reduced from 10 to 0.8 kV, the working distance decreased from 9 to 3 mm and the RBS detector was replaced by an Inlens detector, the spheres vanished and some precipitates appeared in this area. When the measurement at 0.8 kV moved to the position of about 15 mm from the rim, many precipitates were observed, which are interpreted as the condensation products from the evaporation species as shown in figure 5d. With increasing voltage and changing to RBS detector no spheres were detected under the surface in this area. This means that the re-melting induced local phase separation is the origin of the potential local cloudiness. The precipitates on the surface may give rise to localized differences in chemical composition and result in different resistance to attack by various media. However, this area in this study is not cloudy yet. It is possible that the cloudiness in this area occurs later than that in the mouth rim region. In the middle position of the wine cup as shown in figure 5e, there are typical thin dendritic corrosion products, which were observed by Inlens detector at 0.8 kV at 3 mm working distance. With increasing the voltage the morphology was hidden from view. They are corrosion products exposed to humid air and exist within the gel layer on the glass surface. There are many research reports on these phenomena [e.g. 7 to 9]. The corrosion products are formed by ion exchange of H_3O^+ with Na^+ or K^+ in the glass. During this process the glass network can be dissolved [10] and the durability of the whole surface can be reduced. In the stage presented in figure 5e, however, the glass quality is not yet affected irreversibly.











Figures 5a to e. FE-SEM investigations on the surface of a lead crystal wine cup at different positions from the rim, after re-melting the rim without dishwashing and storing in air over one year; a) positions investigated on wine cup, b) and c) measurement within 3 to 5 mm distance from the rim, reveals the morphology of phase separation (10 kV, RBSD, 9 mm working distance), d) measurement within 9 to 15 mm distance from the rim, reveals the area with condensation products of the ion evaporation, e) measurement at over 20 mm distance from the rim in the middle area of the cup, reveals the undisturbed surface with corrosion products caused by exposure to air for a long time. (figures 5d and e were taken at 0.8 kV, Inlens detector and 3 mm working distance).

4. Conclusion

It is shown that the local clouding of some glass articles is related to phase separation induced by after-treatment with flame. Condensation products from evaporation species were observed and dendritic thin corrosion products were detected on the original glass surface. Both features occur at larger distance from the rim than the mouth rim clouding.

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