

Manufacturing-induced surface contaminations

Water absorption of optical glass surfaces induced by classical bound abrasive grinding

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1 Introduction

Classical optics manufacturing is realised by several successive steps. Primarily, preforms of optical components are usually cut from glass blocks or bars using circular saws. The glass component is then shaped by pre-grinding or roughening, and the optically active surfaces are further smoothed by different grinding or lapping steps. Finally, such surfaces are polished in order to generate the actual refractive interface [1]. Throughout the entire process of classical optics manufacturing, aqueous operating materials are used: During cutting and grinding with bound abrasives, lubricants that consist of water and mineral oil are applied to the surface. Lapping – also referred to as loose abrasive grinding [2] – is performed by a slurry, i.e. a mixture of water and lapping grains such as corundum, aluminium oxide or silicon carbide. This process is quite comparable to subsequent polishing where an aqueous suspension is used. Here, water is mixed with polishing agents as for example cerium oxide, iron oxide or zirconium oxide.

The surface of any classically manufactured optical component is thus in permanent direct contact with water in the course of the entire manufacturing process which may last for several hours, depending on the size etc. of the component. Moreover, each single process step and especially grinding and lapping comes along with the formation of micro cracks and subsurface damages [1,3]. The depth of such defects depends on the grain size and can reach some hundreds of microns [4]. The goal of each grinding or lapping step is thus not only to reduce surface roughness, but also the penetration depth of damages by reducing the grain size successively.



Bound abrasive grinding of a glass plate (top) using an abrasive disc (bottom) and an aqueous cooling lubricant.

In the context of this work, the potential function of surface and subsurface damages as reservoirs or cavities for the accumulation of water is of specific interest. As reported by *Bennett* and co-workers, micro cracks allow the inclusion of water and hydroxyl groups (OH^-) into the glass surface and can thus form initiation sites for laser-induced

damage [5]. Apart from the function as reservoir, the presence of cracks and other depressions on the glass surface lead to an increase in effective surface area. This supports another mechanism of water accumulation within the near-surface glass material, diffusion [6,7]. Due to friction between the particular tools and the surface, compar-

SUMMARY

In the course of classical optics manufacturing glass components are in permanent direct contact with aqueous operating materials. Such contact leads to a certain absorption of water and hydrogenous compounds that may induce severe glass defects. In this contribution, absorption of hydrogen and other contaminants during grinding of glass was observed and qualitatively detected via laser-induced breakdown spectroscopy. It is shown that hydrogen, calcium, magnesium, and carbon are implanted into the glass surface where the contaminant

concentration increases over grinding time or contact time of the glass surface with water and the grinding tool, respectively. The contaminants hydrogen, calcium, and magnesium can be attributed to the water used as lubricant. In contrast, carbon most likely originates from wear debris of the used silicon carbide grinding pads. Several possible mechanisms that lead to such surface contamination of glasses during grinding – diffusion, accumulation in micro cracks as well as the formation of hydrated silica – are finally introduced.

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tively high local temperatures that further advance diffusion of water into the glass can arise, supporting this effect by an increase in the diffusion coefficient. Finally, micro cracks can attract water by capillary forces which is known as capillary water absorption (CWA).

The presence of water can lead to severe structural changes of glass [8]. Such changes can be initiated by hydrolytic scission, i.e. a chemical decomposition of the glass network former silicon dioxide [9]. Because of such decomposition, a modified glass layer is generated at the surface. This layer basically consists of silanol (Si-O-H) [10,11] and is thus also referred to as hydrated silica or silica gel. Even though such layers mainly occur during polishing in optics manufacturing, the reaction of silicon dioxide and hydrogen to silanol also takes place during each manufacturing step where the glass surface is in contact with water. The formed layers are known to be capable of inducing a leaching of essential glass constituents from the subjacent bulk material [12]. Moreover, the hydrated silica layer is strongly hygroscopic. This property can cause a deferred glass corrosion, i.e. the formation of a greyish haze at the glass surface in the course of time [1]. Water-induced leaching of glass constituents is also known for the

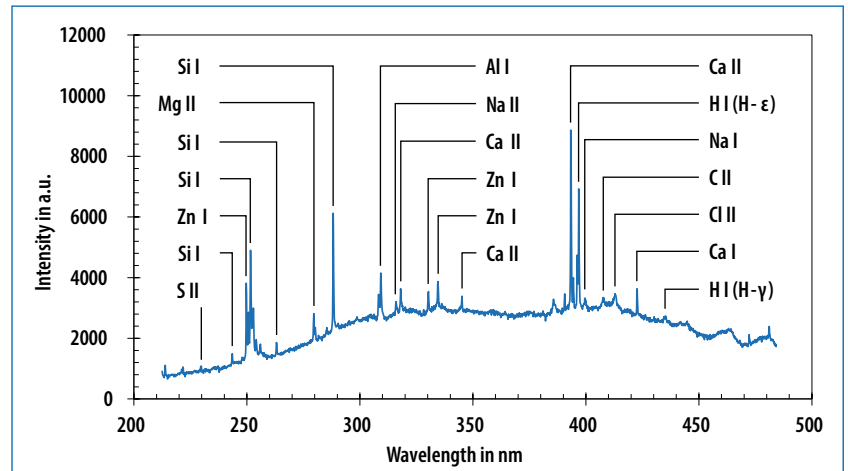


FIGURE 1: Survey spectrum of zinc crown glass, taken by single pulse LIBS at a surface after grinding with an F320 silicon carbide grinding pad for ten minutes.

direct interaction of water molecules and glass where mainly the alkali metals, i.e. the glass network modifiers are affected [13]. The contact of a surface with water may thus lead to a chemical modification of deeper regions within the glass bulk. Water is further capable of forming optically active defects such as hydrogen centres (H(I)-centres) with absorption bands in the ultraviolet wavelength range [14]. Such absorption bands can also be formed due to a water- or hydrogen-induced chemical reduction of silicon dioxide to sub-stoichiometric silicon oxide [15,16]. In terms of mechanical aspects, water may

finally cause a reduction in mechanical stability due to hydrogen embrittlement [17].

Given the extraordinary number of disadvantageous material modifications that can be induced by the presence of water and hydrogen in glasses, the effect of water absorption of optical glass during grinding was qualitatively detected via laser-induced breakdown spectroscopy in this work.

2 Materials and Methods

2.1 Sample preparation

The detection of water absorption of glass during grinding was performed on samples made of zinc crown glass (N-ZK7 from Schott AG). This type of glass was chosen since it is a well-established standard glass for the production of optical components and systems. According to the manufacturer's data sheet the main compounds of this glass are silicon oxide, boron oxide, zinc oxide, aluminium oxide, and sodium oxide where some further traces of calcium oxide, antimony trioxide, and chlorine are added.

Plane samples made of this glass were prepared by cutting plates from a glass block where a conventional circular saw with a diamond-coated saw blade was applied. Subsequently, the surfaces were ground using a commercial grinding machine (TegraPol-31 from Struers GmbH) where the actual grinding tools were silicon carbide grinding pads with different grain sizes. For rough grinding, F320 pads were applied. Medium grinding was

ZUSAMMENFASSUNG

Fertigungsinduzierte Oberflächenkontaminationen – Wasseraufnahme an optischen Glasoberflächen durch konventionelles Schleifen

Während des klassischen feinoptischen Fertigungsprozesses befinden sich optische Komponenten in permanenten Kontakt mit wasserbasierten Betriebsstoffen. Dieser Kontakt führt zu einer gewissen Aufnahme von Wasser und wasserstoffhaltigen Verbindungen, die schwerwiegende Glasdefekte hervorrufen können. In diesem Beitrag wurde die Absorption von Wasserstoff und anderen Kontaminationen während des Schleifens von Glas beobachtet. Das hierbei zur qualitativen Messung eingesetzte Verfahren war die Laserinduzierte Ionisationsspektroskopie. Es wird gezeigt, dass neben Wasserstoff auch Kalzium, Magnesium und Kohlenstoff in die Glasoberflächen eingebracht werden,

wobei die jeweilige Konzentration der Kontaminationen mit der Schleifdauer und der damit einhergehenden Kontaktzeit der Glasoberfläche mit Wasser und dem Schleifwerkzeug ansteigt. Die Verunreinigungen Wasserstoff, Kalzium und Magnesium können dem Kühlschmiermittel Wasser zugeschrieben werden. Kohlenstoff wird aller Wahrscheinlichkeit nach hingegen durch Abrieb der verwendeten Siliziumkarbid-Schleifwerkzeuge eingebracht. Mehrere mögliche Mechanismen, die die beobachteten Oberflächenverunreinigungen während des Schleifens erklären – Diffusion, Anlagerung in Mikrorissen und die Bildung einer Kieselgelschicht, werden abschließend aufgeführt.

performed with F500 pads, and F1200 pads were finally used for fine grinding. According to the FEPA standard, this denomination gives both the material and the mean size of the abrasive grains. The letter "F" stands for silicon carbide where the numbers 320, 500, and 1200 correspond to a mean grain size of 29, 13, and 3 μm , respectively. Each grinding step was carried out for ten minutes in total where the rotation velocity of the tool spindle was 150 rpm. In the course of the entire grinding process, pure tap water was used as lubricant/cooling agent.

2.2 Measurement and evaluation

After each grinding step, the chemical composition of the glass surface was qualitatively measured via laser-induced breakdown spectroscopy (LIBS). Here, a marginal amount of solid material is vaporised by a focussed laser beam, leading to the formation of a light-emitting plasma. The plasma emission spectrum is then recorded and evaluated by comparing the measured data to existing databases. This comparison allows for the identification of single elements within the vapourised sample volume and the determination of its chemical composition, respectively. In the present work, this evaluation was performed with the aid of the freely accessible Atomic Spectra Database provided by the US-American National Institute of Standards and Technology (NIST) [18]. For the actual experiments, i.e. the recording of laser-induced spectra, a commercial automated LIBS apparatus (FiberLIBS from Secopta) was used. Depth-resolved measurements were realised by applying single pulses successively at the same site in order to gain information on the penetration depth of water into the glass surface. The depth of the laser-ablated craters was measured after each laser pulse using a tactile profilometer (Dektak 150 from Veeco). The mean ablation depth and thus information depth per applied laser pulse was about 500 nm. This measurement device was also applied for the determination of the surface roughness after each grinding step.

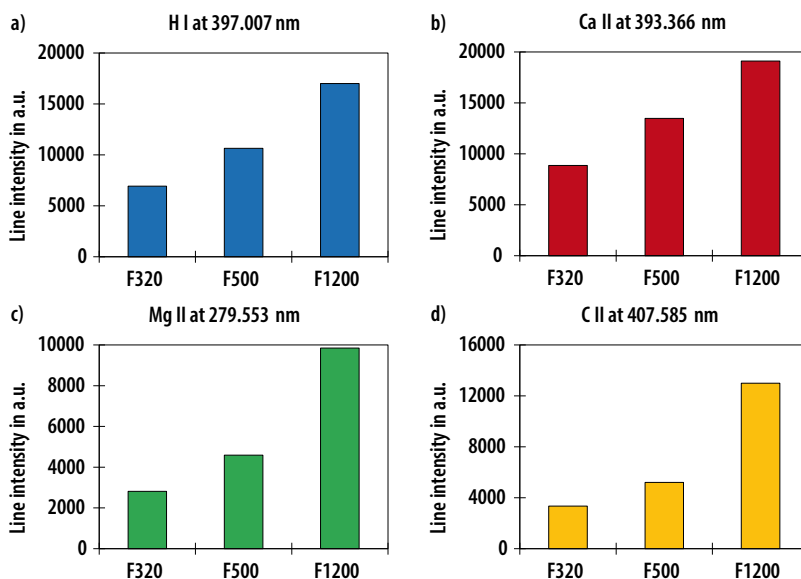


FIGURE 2: Line intensity for selected elements measured for the first laser shots vs. grinding pad denomination (F320, F500, and F1200).

3 Results and discussions

3.1 Identification and origin of contaminants

The survey spectrum of zinc crown glass detected by applying a single laser pulse is shown in Fig. 1. The glass surface measured here was ground with an F320 silicon carbide grinding pad for ten minutes.

In this survey spectrum, characteristic lines of glass constituents from the bulk material can be observed. This includes the spectral emission lines of silicon, zinc, aluminium, sodium, calcium, and chlorine. Moreover, further spectral lines of other elements were detected, including hydrogen, magnesium, sulphur, and carbon. The presence of these elements – and hydrogen in particular – can be attributed to the manufacturing process where water was used as cooling agent. Especially magnesium and sulphur are not constituents of the investigated glass. However, these elements are found in the tap water used for sample preparation as listed in the official drinking water analysis that was performed and provided by the supplier. According to this analysis, the water also contains a notable amount of calcium. The presence of these elements was also verified by LIBS analysis of the used tap water. Here, the same lines for magnesium, calcium, hydrogen, sulphur and sodium as detected in the spectrum taken for

the zinc crown glass, see Fig. 1, were identified.

In contrast to the spectrum taken for water, a clear signal for singly ionised carbon at a wavelength of 407.585 nm can be found in the survey spectrum measured on the glass surface. Since carbon is nominally not existent in the investigated glass and the used tap water (where carbonaceous contaminations may most probably exist, however), the presence of carbon after cutting and grinding is most likely due to contaminations by the manufacturing process. Here, a diamond-coated saw blade and a silicon carbide grinding pad were used. The observed carbon content can thus be attributed to wear debris from the used tools. Surface contamination by residues from cleaning agents such as ethanol or acetone as observed in previous work [16] can be excluded since the samples were not cleaned, but only dried after grinding and prior to the LIBS measurements.

Element	Line wavelength in nm	Ion/atom	Reference
Hydrogen	397.007	H I (H- ϵ)	[19]
Calcium	393.366	Ca II	[20]
Magnesium	279.553	Mg II	[21]
Carbon	407.585	C II	[22]

TABLE 1: Selected elements and the corresponding emission lines chosen for further examination of water absorption of the investigated zinc crown glass during grinding.

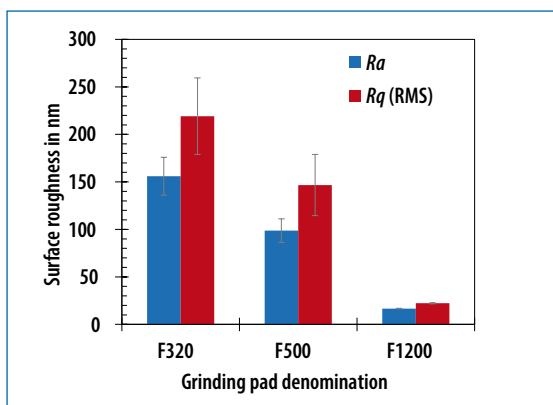


FIGURE 3: Arithmetic mean roughness R_a and quadratic mean roughness R_q (RMS) of ground zinc crown glass surfaces vs. grinding pad denomination.

3.2 Depth-distribution and time-dependency of contaminants

For further examination of water absorption during grinding, selected lines that featured the most significant changes in intensity were chosen. As listed in Table 1, this includes three main elements from the tap water, hydrogen, calcium, and magnesium. In addition, carbon was considered because this element is not found in the glass bulk material. According to the manufacturers data sheet, merely marginal amounts of calcium are found in the glass whereas the other considered elements should not be existent.

Depth-resolved measurements were performed with focus on these four lines where two general interrelationships were observed: First, for each

element, a high line intensity was found directly at the sample surface, i.e. for the first measuring laser pulse. With increasing depth or number of laser pulses, the line intensity and contaminant concentration, respectively, decreased and the curves flattened quite rapidly, approaching a final value at a depth of some microns. Such behaviour of the depth-dependency of manufacturing-induced contaminants in glass surfaces such as water or residues from polishing agents was also observed and reported in the past [23–26]. Second, a certain correlation of the line intensity level and the grinding pad denomination was observed. With increasing denomination and decreasing grinding grain size, respectively, the line intensity increased generally. The results indicate that the grinding process has led to a contamination of the outermost surface as shown by the comparison of the particular line intensities measured for the first laser shots shown in Fig. 2.

This behaviour implies that the observed absorption of water and related elements is probably not only due to accumulation and inclusion of the cooling agent in micro cracks and subsurface damages. As already mentioned in the introduction, both the micro crack depth and the depth of subsurface damages are directly related to the mean grinding grain size and surface roughness, respectively. Since a higher value in the grinding

pad denomination results in a smaller grain size and surface roughness as shown in Fig. 3, the size and number of cavities and capillaries for accumulation of water continuously decreases in the course of the entire grinding process.

The inclusion of water is thus most likely driven by another mechanism or other mechanisms. In order to identify such possible interactions the time-dependency of the absorption of grinding-induced contaminants, i.e. elements from water and carbon was measured. For this purpose, zinc crown samples were ground successively using an F500 silicon carbide grinding pad and LIBS spectra of the ground surface were taken after a time interval of one minute. The results are shown in Fig. 4.

It turns out that the surface is continuously contaminated by the considered elements in the course of grinding time and the accompanying reduction in surface roughness, respectively. This observation supports the assumption that a sheer accumulation of water and wear debris from the grinding pad within cracks or digs is not the only or main mechanism that leads to contamination. Instead, surface contamination increases over grinding time. The longer the grinding process the more elements from the lubricant (water) and the grinding tool (wear debris from silicon carbide) are implanted into the surface. However, one has to consider that the observed contamination approaches a saturation value. Actually, the rise shown in Fig. 2 could be explained by the fact that successive grinding with decreasing grain size is equivalent to an increase in effective machining time, i.e. contact time of the glass surface with the used cooling lubricant, water. Against this background, two strongly time-dependent and near-surface effects can be considered: First, diffusion of water into the glass that was already investigated and reported by various authors [6–8,27,28] leads to a transport of both hydrogen and traces from the water into the surface. Second, such traces are also embedded within the hydrogenous layer that is formed by the interaction of water with silicon dioxide from the glass network. Even though this effect is mainly examined and discussed for polished glass surfaces in literature, it can also occur in the course of grinding.

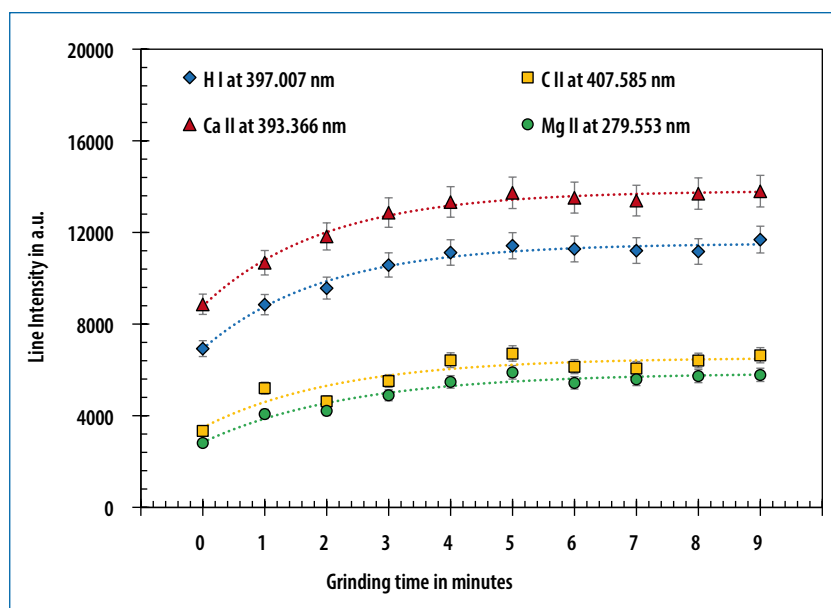


FIGURE 4: Line intensity of selected elements on zinc crown glass ground by a F500 silicon carbide grinding pad vs. grinding time.

4 Conclusions

The impurities in ground glass as detected in this work can partially be attributed to the water used as lubricant during grinding. As shown by reference data and comparative measurements, hydrogen, calcium, and magnesium are found in the water whereas carbon contamination seems to originate from wear debris of the used grinding tools. The penetration depth of the contaminants is up to some microns. It was further shown that surface contamination is time-dependent: the longer the grinding time, the higher the amount of contaminants or – strictly speaking – the higher the intensity of the emission line of the particular element.

It can be assumed that the observed near-surface contamination by elements from the tap water and pads used for grinding is most likely due to the combination of several effects: First, a certain accumulation of contaminants such as wear debris of the used tools in geometrical surface defects as for example digs, holes, scratches and subsurface damage. Second, diffusion of water and contained elements, e.g. magnesium or calcium into the glass surface. Third, the formation of hydrated silica within surface defects and on top of the surface, embedding traces from the water as well as other impurities.

Based on the findings it can be stated that in the course of classical manufac-

turing grinding does not only lead to the aimed and advantageous decrease in surface roughness, but may also give rise to a certain increase in surface contamination. This effect causes an alteration in chemical composition of ground glass surfaces and thus a modification of the subsequent polishing process, which includes a considerable chemical component. It can finally be assumed that the chemical interaction of the polishing slurry with the glass surface depends on the operating materials and tools used during previous grinding or lapping steps. The interaction of impurities induced by the grinding process and the polishing slurry may give rise to further secondary surface contaminations during polishing. Especially for sensitive glasses such as fluorine crown glasses, this point is of interest for the production of polished surfaces with high cleanliness.

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