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Faculty of Mechanical Engineering



PROSPECTS IN MECHANICAL ENGINEERING

8 - 12 September 2008

www.tu-ilmenau.de



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http://www.db-thueringen.de/servlets/DocumentServlet?id=17534

Published by Impressum

Publisher Der Rektor der Technischen Universität Ilmenau

Herausgeber Univ.-Prof. Dr. rer. nat. habil. Dr. h. c. Prof. h. c. Peter Scharff

Editor Referat Marketing und Studentische Angelegenheiten

Redaktion Andrea Schneider

Fakultät für Maschinenbau

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Editorial Deadline Redaktionsschluss

17. August 2008

Publishing House

Verlag

Verlag ISLE, Betriebsstätte des ISLE e.V. Werner-von-Siemens-Str. 16, 98693 Ilmenau

CD-ROM-Version:

Implementation Technische Universität Ilmenau Realisierung Christian Weigel, Helge Drumm

Production Herstellung CDA Datenträger Albrechts GmbH, 98529 Suhl/Albrechts

ISBN: 978-3-938843-40-6 (CD-ROM-Version)

Online-Version:

Implementation Universitätsbibliothek Ilmenau

Realisierung ilmedia

Postfach 10 05 65 98684 Ilmenau

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Polishing process of optical glasses / Simulation of the chemical influences

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Abstract

In the last step of fabrication, optical and fine-optical glasses are polished to fulfill the optical requirements for their surfaces. The major influences on the process are caused by the mechanics of the polishing machine, by the chemistry (composition of the glass, as well as the polishing suspension of water and polishing grains, CeO₂) [1], [2] and by the material and structure of the polishing pad.

From previous own results [3], [4] it is known that the stability of the colloidal system has a major impact on the polishing results and that it is influenced by matter from the glass removal. Thus the glasses have been classified in glass families, depending on their chemical composition and their mutual compatibility in the process. As it is not always possible to measure this compatibility, the impact of the various dissolved glass ions in the fluid phase of the polishing suspension is simulated by the use of thermodynamic parameters. Therefore the specific solubility products in the aqueous phase are modeled (using, e.g., the software HSC) comprising steady accumulation of ions from the glass removal.

With this simulation, the examination of the chemical part of the chemo-mechanical polishing process will be concluded.

Introduction

Chemical-mechanical polishing (CMP) is the final step in the production of many optical glasses. This process is employed to bring about the desired surface quality (minimum roughness, absence of surface and sub-surface flaws) as well as the final adjustment to the macroscopic shape for optical applications, for both of which a certain removal of glass material is necessary. Polyurethane foam was used as polishing pad and a suspension of a fine commercial CeO₂ powder was used as polishing agent. Apart from the mechanics of the polishing machine [5], [6] and the polishing grain substrate [7], the chemistry of the polishing suspension has a major impact on the polishing result. Earlier own results from polishing experiments showed that the stability of the colloidal system of the polishing suspension is influenced by the amount and chemical composition of matter removed from the glass and dissolved in the polishing suspension.

Earlier own results

The polishing process of optical lenses strongly depends on the glass composition and on the interaction between different kinds of glass which are polished consecutively. Consecutive polishing of different kinds of glass is a common method in optical technology to save resources (polishing suspension) and time (cleaning and changing). To classify this dependency systematically, the discussed glasses were divided into "glass families" (Table 1), depending on the composition and on their polishing behavior.

Table 1. Glass families

Family	Glass	Composition
1	SF 6	SiO ₂ -rich,
	N-SK 16	CaO-poor
2		SiO ₂ -rich,
	N-LaK 8	CaO-containing
2a	N-FK 51	like 2, but fluoride glass.

Within one glass family, polishing glasses in a mixed sequence does not cause any problems, but if glasses from different families are polished consecutively, problems may occur. To determine such chemical influences to the polishing process, chemical additions were made during the polishing process of individual glasses. The removal of glasses per time, and the surface quality directly depended on such additions.

For example, the equilibria between Si, Ca and Zn ions are very sensitive and a shift of these equilibria can cause big differences in the removal rates. A well pre-conditioned suspension yielding good polishing results requires a certain amount of dissolved matter, which corresponds to a specific solubility product depending on the glass to be polished. Beyond a certain limit, however, this balance is tipped, yielding bad results. Another example is the unacceptably high roughness which is initiated by the critical presence of fluoride and alkaline earths in the polishing suspension at low pH values. It was assumed that the formation of CaF₂ causes this high roughness. This effect does not appear at high pH values, as alkaline earth fluorides are stable within a wide pH range, but at high pH values they become instable. To indicate the reasons for the observed behavior in the polishing process, a simulation of the chemical influences to the polishing process was realized.

Simulation of chemical processes in aqueous solution

To examine the complex chemical processes in the aqueous solution (polishing suspension), the polishing process is modeled with the software HSC Chemistry from Outokumpu. Therefore the removal in the polishing process is simulated by a thin glass layer, which is thought to be dissolved in water (Fig. 1 for glass 1). Thus a reaction path for the interaction of the specific glass ions in the polishing suspension can be made. Simulating the polishing process this way, means to simulate only the chemical part of the process, the mechanical part (contact pressure of the polishing tool etc.) or the influences of the polishing pad are not considered. As seen in Fig. 1, it is possible to take the chemical additives into the simulation or to model the interaction between two kinds of glass.

To model the dissolution of a certain glass in aqueous solution, the composition must be known. The concentration of certain species in the aqueous solution can be applied as a function of the amount of dissolved glass (removed from the polished glass).

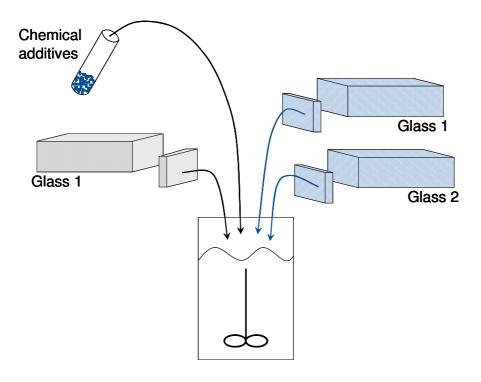


Figure 1. Schematic diagram of the dissolution of different glasses and chemical additives in water (polishing suspension) as modeled by thermodynamic modeling of the aqueous system

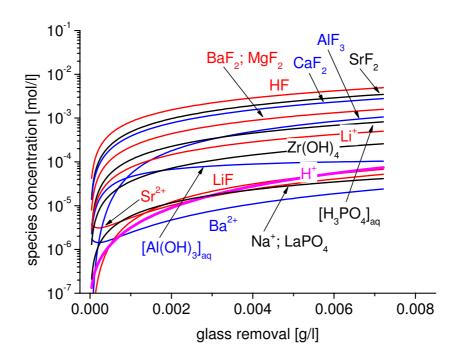


Figure 2. Concentration of species in aqueous solution as a function of the amount of dissolved glass (removed from the polished glass) for a typical optical fluoride glass

The remarkable example of a typical optical fluoride glass mentioned above was modeled first, see Fig. 2. First, the pH value, the negative species concentration of H⁺, declines to 6 due to the dissolution of the glass. In earlier polishing tests it was found, that each glass causes a specific pH value, this phenomenon can now be modeled, producing the exact pH value.

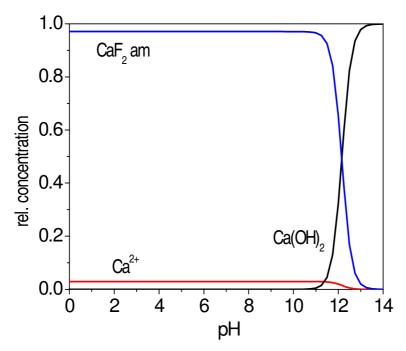


Figure 3. Stability of calcium fluoride as a function of the pH value

It can be seen, that Ca^{2+} and Mg^{2+} form fluorides after a short polishing time and Sr^{2+} and Ba^{2+} after some more time. So, the equilibria in the polishing suspension will shift to the fluorides, when the concentration of species reaches the limit of solubility.

As known from Kaller [8], the best polishing grains are softer than the polished surface and do not mechanically remove material. Though the fluorides are not the polishing grain, they can damage the glass surface by scratching, as they form hard, insoluble crystals. This assumption is supported by the practice in the optical technology, where fluoride glasses are often handled in a particular way, even without this knowledge. To the polishing suspension special additions are made, probably to avoid the formation of fluorides after longer polishing time. For example the pH value is raised. As known from own experiments, alkaline earth fluorides become instable at high pH values. In Fig. 3, as an example, the stability of CaF₂ is plotted as function of the pH value. It is easily seen that the CaF₂ crystal is stable at pH values below 11 and becomes unstable at

higher pH values.

Another deposit is gibbsite, a soft and fine crystallite, which will not scratch but can form a fog on the glass surface; this fog can be removed by washing the lenses, after the process.

In Fig. 4 the same modeling for the fluoride glass with addition of CaCl₂ is presented. In this simulation, the specific pH value is 5 and it is not reached directly after starting the polishing process, as was the case without CaCl₂. The excess of the solubility product directly causes a deposition of CaF₂, the amount of F- is much smaller than in the modeling without CaCl₂ addition. CaF₂ is the only precipitation over a long polishing time. As mentioned above, it forms hard crystals. In earlier polishing experiments it was observed, that the addition of CaCl₂ to the polishing process of this fluoride glasses causes big surface roughness, which means poor surface quality. It was assumed, that this is due to the precipitation of CaF₂. By the modeling it is shown, that this assumption was right, but it leaves to check if the precipitation takes place on the glass surface and causes this roughness because of a sporadic growth or if it precipitates in the aqueous solution and scratches the glass surface. From experiments it is known, that the negative influence of the CaCl₂ can be eliminated by raising the pH value, as explained above. From the experiments and the following modeling it was learnt, that glasses containing alkaline earth should not be polished in sequence with fluoride glasses. Alternatively, a method, like the raising of the pH-value must be found to avoid the negative influence. Anyway, the pH-value has to be checked continuously, as for every glass exists a specific pH value which will be leveled after a short polishing time. Like this example, a reaction approach for the specific glass ions of each discussed glass will be made. The interaction with other polished glasses will be examined, like shown in Fig. 1 on the right side, to control the division into the "glass families". The concept of reaction path modeling is extended to other combinations of glass compositions with less obvious interactions than the formation and precipitation of fluorites. Concepts for the stabilization of the polishing process are outlined. The use of organic complexing agents is recommended to influence critical solubility equilibria. By this modeling the chemical reactions in the aqueous solution can be forecasted, but

the mean to the polishing process must be verified in polishing experiments.

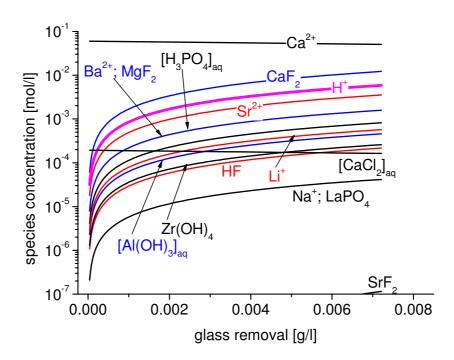


Figure 4. Concentration of species in aqueous solution as a function of the amount of dissolved glass (removed from the polished glass) for a typical optical fluoride glass with the prior addition of CaCl2

The research project (AiF-Nr. 14741N) was financed within the agenda for promotion of industrial collective research (IGF) by the Bundesministerium für Wirtschaft und Technologie via the Arbeitsgemeinschaft industrieller Forschungsvereinigung (AiF) and the Forschungsvereinigung Feinmechanik, Optik und Medizintechnik (F.O.M.).

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