Nanocomposite glass abrasives

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Cerium oxide is a suitable material for glass polishing because it has both a high chemical reactivity and a suitable hardness for glass polishing. We focused on nano-dispersion abrasives containing two materials that specialize in a chemical reactivity with glass and a suitable mechanical strength and they were synthesized by spray pyrolysis. We first review on CeO₂–ZrO₂–Y₂O₃ nano-composite abrasives that can show you the effect of nano-composition on glass polishing. These nano-composites showed slightly lower removal rate than commercial CeO₂-based abrasive, but the composite led to smooth surface of glass. The nano-dispersed SrZrO₃/ZrO₂ composite particles were then synthesized by spray pyrolysis. The glass polishing using SrZrO₃/ZrO₂ nano-composite abrasives led to relatively high removal rate and quite smooth surface of glass. The SrZrO₃/CeO₂ abrasives showed superior polishing properties to conventional ceria-based abrasives by adjusting SrZrO₃/CeO₂ ratios. These results revealed that the nano-composition enables us to control mechanical and chemical ratios and this CMP control would lead to develop leading-edge abrasives.

1. Introduction

Cerium oxide (ceria) abrasives are widely used for precise polishing of glasses, and precisely polished glasses with the ceria-based abrasive are used as hard disk substrates and flat panel displays. The polishing with ceria-based abrasives achieves higher removal rate as well as quite smooth surface. The mechanism of glass polishing with ceria-based abrasives had some theories; (1) micro cutting theory, (2) plastic flow theory, (3) chemical reaction theory, etc. Micro cutting theory suggested that fine abrasives crashed during rotating glass and polishing pad under some loads could polish glasses mechanically, but this theory cannot explain polishing results that relatively large abrasives with a diameter of 1μm result in very smooth surfaces of glass with the average surface roughness, Ra of several nm. Plastic flow theory suggested that heat generated by friction during rotating them under some loads could partly melt the surface of glasses and flattened. Dr. Izumitani claimed glass plastic flow theory cannot completely explain glass polishing since removal rates of glass polishing had no correlation with softening temperatures. Chemical reaction theory suggested that surface of glass are softened by some chemical reactions during polishing. The detail of chemical reactions is not clarified yet, but chemical reactions at the atomic level would be essential to obtain very smooth surfaces of glasses.

These excellent polishing properties of the ceria-based abrasive are brought by chemical mechanical polishing (CMP)³⁴ which is attributed to a high chemical reactivity with glass surface and a suitable hardness. Some simple oxides such as Al₂O₃, SiO₂ or ZrO₂ reveal relatively low polishing properties for glasses. The low properties are considered due to poor chemical reactivity with glass in spite of high mechanical strength.

Pure ceria particles also exhibit low polishing properties, but polishing rate with commercial ceria-based abrasives achieve excellent properties. Commercial ceria abrasives contain lanthanum at a molar ratio of 20–30% because a mineral of ceria, such as bastnesite, involved much amount of lanthanum salts and it costs to remove lanthanum from bastnesite (Fig. 1). Experimental results also clarified that the dissolution of lanthanum in ceria much improves removal rate.⁵⁶⁷ Oxygen defects are formed by dissolving lanthanum in ceria. The effect of lanthanum on mechanical strength would be negligible for CMP properties. The effects of oxygen defect in ceria on chemical polishing properties were thus investigated using computer simulations.

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Dissolution of lanthanum in ceria enhances diffusion of oxygen in ceria via oxygen defects. The simulation revealed that oxygen atom would be more stable in ceria bulk than at the surface and some oxygen atoms at the surface of ceria transfer to the bulk under the relatively high oxygen diffusion constants. The transfer of oxygen from surface to bulk leads to expose cerium atoms to the surface of the particles. The exposed cerium that has trivalent cations easily supplies electron to chemical bonds of glasses. The hydrolysis induced by electron transferred to several furnaces by flowing air at the rate of 1.0–3.0 dm$^3$ min$^{-1}$. The furnaces were arranged in a row to allow mist to heat gradually. Generally adequate conditions of SP process results in homogeneous spherical particles with the diameter of about 0.5 to 1.5 μm and narrow particle size distribution since the obtained particle sizes are reflected by droplet size of atomized mists (Fig. 3).\cite{11,12}

3. CeO$_2$–ZrO$_2$–Y$_2$O$_3$ nanocomposite abrasive\cite{13}

High performance in glass polishing is required CMP effects that make a good balance of chemical polishing and mechanical polishing. Cation-doped ceria is considered to have the relatively good balance for CMP, but it was difficult to clarify a guideline for developing novel well-balanced CMP materials because of poor quantitative data on CMP. We then tried to combine chemically active materials and mechanical materials at several tens or hundreds nano-meter scales. We then refer the combined abrasives at nano-meter scales to “nanocomposite abrasives” according to the definition of nanocomposite as a multiphase solid material where one of the phases has one, two or three dimensions of less than several hundred nanometers, or structures having nano-scale repeat distances between the different phases that make up the material.\cite{14}

Ceria shows chemical and mechanical polishing properties and zirconia has sufficient mechanical strength, and the theses properties would be enhanced by dissolving yttrium. We then prepared ceria/zirconia nanocomposites to investigate effects of chemical/mechanical composites on polishing properties. Yttrium-doped ceria (YDC) would possess relatively high chemical polishing properties because YDC showed higher removal rate than lanthanum doped ceria. Yttrium doped zirconia (YSZ) was used as a mechanical polishing material. Whether YSZ achieves chemical polishing or not is still controversial, but YSZ clearly shows much higher mechanical than chemical polishing properties. We then prepare YDC/YSZ nano-composite particles by SP. Both YDC and YSZ have flutore crystal structure, but they are not compatible with each other by firing at less than 1000°C and yttrium can be easily dissolved into both zirconia and ceria. An adequate SP condition using solution mixed with cerium, zirconium and yttrium salts resulted in YDC/YSZ nano-composite particles with average particle diameter of 0.8 μm and the particle sizes and size distribution was almost independent of YDC/YSZ ratios (Fig. 4). The composite particles were constituted by YSZ and YDC primary particles with the average

\[ d = 0.34 \sqrt{\frac{8\pi \gamma}{\delta f^2}} \]  \hspace{1cm} (1)

where $d$ is a mean size of droplets, $\delta$ is a density of an atomizing solution, $\gamma$ is a surface tension of a solution, and $f$ is an oscillation frequency of an ultrasonic atomizer. The size of droplets can be controlled by adjusting the ratio of density to surface tension of water solution. Practically, water solution dissolved with various nitrates was atomized using an ultrasonic generator with an oscillation frequency of 1.7 MHz. Atomized mist was then transferred to several furnaces by flowing air at the rate of 1.0–3.0 dm$^3$ min$^{-1}$. The furnaces were arranged in a row to allow mist to heat gradually. Generally adequate conditions of SP process results in homogeneous spherical particles with the diameter of about 0.5 to 1.5 μm and narrow particle size distribution since the obtained particle sizes are reflected by droplet size of atomized mists (Fig. 3).\cite{11,12}
diameter of 10–30 nm. The YDC/YSZ slurry were prepared by dispersing the nano-composite particles in water and polishing properties of glass were investigated with the slurry. Figure 5 shows the relationship between removal rate and composition ratios. YDC showed comparable removal rate to commercial ceria-based abrasives, whereas YSZ would achieve good mechanical polishing but removal rate of YSZ was less than one third as compared to the rate of YDC. The 50/50 composition of YDC/YSZ showed similar removal rate to YDC, and the composite abrasives containing YDC more than 20% achieved similar smooth roughness to YDC. Cation-dissolved ceria would have both high chemical polishing and mechanical polishing, but some researchers claims that the chemical reactivity of cation-dissolved ceria may be higher than mechanical properties as compared to ideal balance of the CMP. The YDC/YSZ composite reveals that YDC would achieve high chemical reactivity since the composite particles containing 80% YSZ still resulted in good surface roughness with no scratching on polished glasses.

4. SrZrO$_3$/ZrO$_2$ nanocomposite abrasive\(^\text{16}^\)\)

Cation-doped ceria would have relatively high chemical polishing properties but chemical reactivity of ceria would be insufficient for a chemical polishing material because the correlation profiles between the removal rate and the composite ratio of YDC/YSZ particles did not observe optimum value. SrZrO$_3$ was found to show unique polishing properties. When borosilicate glass was polished with SrZrO$_3$ particles synthesized by SP and subsequently calcined at 570°C, the glass turned to be opaque. The glass surface seemed to be corroded rather than mechanically scratched, but the removal rate was very small. These results indicated that SrZrO$_3$ has high chemical reactivity with glasses although the origin of chemical reactivity has not been clarified yet.

SrZrO$_3$ would achieve high chemical reactivity but insufficient mechanical strength for CMP. We then used as a chemical polishing material for nanocomposite abrasives and SrZrO$_3$/ZrO$_2$ (SZZ) nano-composite particles were investigated as a novel CMP abrasives. Figure 6 shows SEM images of synthesized particles by SP.\(^\text{17,18}^\) The particles were spherical shapes which reflected the solution droplet generated using an ultrasonic atomizer and average primary grain sizes evaluated from the SEM images were 70–100 nm in diameter. We investigated relationship between abrasive material and polishing property. Figure 7 shows relationship between glass removal rate and abrasive composition. The removal rates of SrZrO$_3$ and ZrO$_2$ abrasives were lower than 200 nm min$^{-1}$. The SZZ nano-composite particles with SrZrO$_3$/ZrO$_2$ ratio of 7/3 (SZZ73) resulted in the maximum removal rate of 450 nm min$^{-1}$, which was approximately 80% of the removal rate with commercial ceria-based abrasive. The removal rate was also evaluated using mixed abrasive of SrZrO$_3$ and ZrO$_2$ particles with the same composition ratio of the composite abrasives. Although the removal rate slightly increased using the mixed abrasives comparing with that of SrZrO$_3$ or ZrO$_2$ abrasives, the removal rates with the mixed abrasives were much lower than those with the nano-composite abrasives. The removal rate with SZZ73 abrasive was twice as high as that with the mixed abrasive. Figure 8 shows average surface roughness, Ra of the glass after polishing as a function of abrasive composition. Polishing with SrZrO$_3$ abrasive resulted in the glass surface of 0.58 nm Ra and the roughness was lower than that with the commercial ceria-based abrasive. The roughness with the nano-composite abrasives was lower than that of 1.07 nm Ra with ZrO$_2$ abrasive. On the other hand, the mixed abrasives resulted in higher roughness than that with the nano-composite abrasives. These results indicated that the microstructure control of particles was of great impor-
for achieving high CMP performance by combination of 
SrZrO$_3$ and ZrO$_2$. The rough surface with the mixed abrasives 
would be mainly caused by ZrO$_2$ abrasive although the mixed 
abrasive was included SrZrO$_3$ abrasive which achieved smooth 
surface.

5. SrZrO$_3$/CeO$_2$ nanocomposite abrasive

Pure ceria shows relatively low polishing properties but cation-
doped ceria such as YDC much improved the properties. The 
doping of yttrium at zirconium sites would increase chemical 
reactivity for polishing but would not alter mechanical strength. 
Pure ceria achieves both chemical polishing and mechanical, 
but mechanical behavior would be relatively strong as compared 
to the ideal valance of CMP. Therefore pure ceria would be also 
acted as mechanical polishing materials. We then prepare nano-
composite abrasives in combination with SrZrO$_3$ as chemical 
reactive material and pure CeO$_2$ as mechanical polishing mate-
rial. SP process enabled us to prepare SrZrO$_3$/CeO$_2$ (SZC) nano-
composite particles. Figure 9 shows SEM images of various 
SZC nano-composite particles. The particles sizes were about 1.0 
µm not depending on compositions, and the primary grain sizes 
of SrZrO$_3$ and CeO$_2$ were almost independent of composition 
ratio. Figure 10 shows the relationship between removal rate 
and composition ratio/ The nano-composition improved removal 
rate as compared to ceria and the removal rate of SZC composite 
was comparable to commercial ceria-based abrasives. Figure 11 
shows surface roughness of glasses, Ra and the composition. The 
composite abrasives improved polishing properties of removal 
rates and surface roughness as compared to SrZrO$_3$ and CeO$_2$. 
The SZC nano-composite particles that contained 50% CeO$_2$ 
achieved comparable removal rate and superior surface rough-
ness of glass to commercial ceria-based abrasives.

6. Advantage of nano-composition for CMP

The main difference between nanocomposite and mixed abra-
sive was a distance between SrZrO$_3$ and ZrO$_2$ or CeO$_2$ grains 
which means a distance between active sites of chemical and 
mechanical polishing. Figure 12 shows schematic illustrations of 
mixed and nano-composite abrasive sites on a glass substrate. 
The distance between chemical and mechanical sites of the mixed 
abrasives can be estimate using average grain sizes, whereas that 
of nanocomposite can be calculated with average primary grain 
sizes. The distance between SrZrO$_3$ and ZrO$_2$ or CeO$_2$ of the 
mixed abrasive sites was estimated to be about 800 nm due to 
particle size of both SrZrO$_3$ and ZrO$_2$ or CeO$_2$ while that of the 
nano-composite abrasive site was about 80 nm. The mechanism 
of CMP was considered that Si–O bond in the glass was softened 
and/or weakened by chemical reaction between the glass and the 
abrasive, and then glass surface was mechanically removed. 
Therefore, it would be necessary that the mechanical polishing 
material has to exist at the softened glass area where the chemi-
cal polishing material chemically reacted with the glass. The
Experimental results indicated that the distance between chemical and mechanical sites of 800 nm would be too large to originate CMP effect while the distance of 80 nm would be appropriate under the CMP polishing conditions. The reason for the optimum distance has not been still vague, but two possible reasons were considered as follows. One possible reason was that the area of softened glass would determine the optimum distance; assuming that the softened area expands to about 80 nm in radius from the contacting point between chemical sites and the glass, the nano-composite abrasive would show CMP effect while the mixed abrasive would not. Another possible reason was that the time for maintaining the softening effect (time constant) would determine the optimum distance. Under the polishing conditions of this study, the traveling times between chemical sites and mechanical sites were estimated as about 700 and about 70 ns for the mixed and nano-composite abrasives, respectively. Assuming that the time constant for glass softening effect by the reaction between a chemical site and the glass is about 70 ns, the nano-composite...
abrasive would show CMP effect while the mixed abrasive would not. The further investigations would be required for understanding the origin of the optimum distance. The nano-dispersed composition that is composed of two different materials would be a promising strategy for leading-edge abrasives.

7. Summary

Advantage of nano-dispersed composition for CMP was reviewed in terms of chemical and mechanical sites. The SrZrO$_3$/CeO$_2$ nano-composite abrasives showed superior polishing properties to conventional ceria-based abrasives by adjusting the ratio of chemical and mechanical materials and the distance between chemical and mechanical sites.

Distinguished CMP would be required to achieve a balance between chemical polishing and mechanical polishing, but it was difficult to estimate the balance quantitatively such as chemical or mechanical polishing quantities and interaction parameters between chemical and mechanical sites. This nano-composition would enable us to estimate these parameters quantitatively and optimizing these quantitative parameters will lead to novel CMP abrasives.

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