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Polishing of Tungsten Carbide by Combination of Anodizing and Silica Slurry Polishing

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Sintered tungsten carbide (WC) is widely used in precision molding of optical glass lenses, and is considered as a critical mold material for optical industry, due to its high hot hardness and low thermal expansion ratio. However, WC is also a well-known difficult-to-polish material owing to its high hardness and strong chemical inertness. In an effort to realize the high-quality and highly efficient polishing of WC, a two-step polishing process combining anodizing and soft abrasive polishing was developed. Experimental studies of the anodizing step and the slurry polishing step were conducted. Anodizing has been found to be able to quickly soften WC and realized a drastic decrease of its surface hardness from 22.1 GPa to below 2.0 GPa, which allows us to polish the substrate surface using soft silica abrasives. In the polishing step using silica slurry, the oxide layer was removed and it has been revealed that the surface quality of polished WC was greatly affected by the duration of anodizing and the type of polishing pad. A scratch-free, pit-free and smooth WC surface can be obtained by combination of 10 min of anodizing and 30 min of silica slurry polishing using a suede type polishing pad. This research offers a new method for achieving high-quality finishing of WC with high efficiency.

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Precision aspheric glass lenses have been used in a variety of industry fields, such as imaging optical systems, astronomical telescopes, high power laser collimators, contact lens manufacturing and so forth. These aspheric glass lenses are mostly manufactured by a glass press molding process with aspheric ceramic molds made of tungsten carbides (WC) or silicon carbide (SiC), and WC is the most widely used mold material for fabrication of low-Tg glass lenses, due to its better grindability in ultra-precision grinding.[1] The quality of these aspheric glass lenses are strongly determined by the quality of the WC molds including their form accuracy, surface roughness, surface integrity and subsurface damage (SSD), which could affect lens demolding process, mold life and optical performance.[2] Hence, to achieve the excellent performance of the WC molds as well as the molded aspheric glass lens, high-quality surface finishing of WC is indispensable.

Currently, WC molds are mostly ground by ultra-precision grinding machines with fine grained diamond wheels. Then, an additional finishing process is conducted to improve the surface roughness, remove the grinding marks and minimize the SSD introduced by the grinding process.[3] Several finishing methods have been applied to polish the ground WC molds such as diamond abrasive polishing,[2] magnetorheological finishing,[4] vibration assisted polishing[5] and electrorheological fluid-assisted polishing.[6] However, in these finishing methods, diamond abrasives are inevitably used due to the high hardness of WC. Thus, micro scratches and additional SSD, which could deteriorate the performance of the molds, are inevitably introduced. Meanwhile, the low material removal rates (MRRs) and the high finishing costs due to the dependence on superior polishing equipment make it costly to finish the WC molds in mass production using these methods. Chemical mechanical polishing (CMP) using silica (SiO_2) slurry has been widely considered as a damage-free finishing method for some hard and brittle materials like glass[7] and semiconductor substrates.[8] However, CMP of WC has not been commercially applied owing to the extremely low MRR. Thus, a new finishing method to realize the damage-free and highly efficient finishing of WC molds is strongly required.

To resolve the above mentioned SSD and MRR issues in finishing of optical WC molds, hybrid polishing combining surface modification and soft abrasive polishing is a promising approach. The surface modification process makes WC soft and greatly improves its machinability while the polishing process only removes the modified layer and realizes good surface finishing without introducing additional SSD. For surface modification of some hard and stable materials like SiC, WC and so forth, several methods like thermal oxidation,[9] laser modification,[10] ultraviolet irradiation,[11] wet chemical reaction[12] and plasma treatment[13] have been widely studied. To combine these modification methods with conventional mechanical material removal, some novel polishing processes have been proposed. As thermal oxidation was conducted under a very high temperature,[9] it is usually difficult to conduct thermal oxidation with abrasive polishing in the same processing zone simultaneously. Laser-assisted polishing[14] has been applied to polish diamond while UV irradiation assisted polishing[11] has been utilized to polish some wide band-gap semiconductor materials. Plasma-assisted polishing,[13] in which plasma based surface modification and soft abrasive polishing are combined, has been successfully developed to polish some hard and brittle materials. Water vapor contained plasma was utilized to oxidize the substrate surface and abrasive polishing removed the oxide layer which was usually much softer than the bulk material. Damage-free and atomically flat surfaces of SiC and GaN have been obtained using plasma-assisted polishing.[15] However, the MRRs of these polishing processes are still greatly limited by the low efficiency of the utilized modification methods.

Anodizing has been widely known as a rapid surface modification method especially for conductive materials like metals.[16] The hybrid polishing process combining anodizing and slurry polishing is called electro-chemical mechanical polishing (ECMP) and has already been studied by several groups.[17] Anodizing can make the workpiece surface soft and ensure the polishing using soft abrasives applicable. Polishing using soft abrasives will only remove the soft modified layer without forming SSD to the bulk. Thus, highly efficient and damage-free finishing can be realized by ECMP. It has been reported that ECMP could also be applied to ceramics like single crystal SiC.[18] A slurry-based ECMP process has been proposed and was applied to 4H-SiC.[19,20] In Deng's work, ceria slurry worked as the electrolyte for anodizing as well as the polishing media for removal of the oxide layer. A high polishing efficiency has been demonstrated and a scratch-free and smooth surface with the root mean square (rms) roughness less than 3 nm was obtained after polishing for only 30 min.

The motivation of this research is to polish WC using ECMP. As a feasibility study, a two-step polishing process, in which anodizing and soft abrasive polishing are separately combined, is applied to

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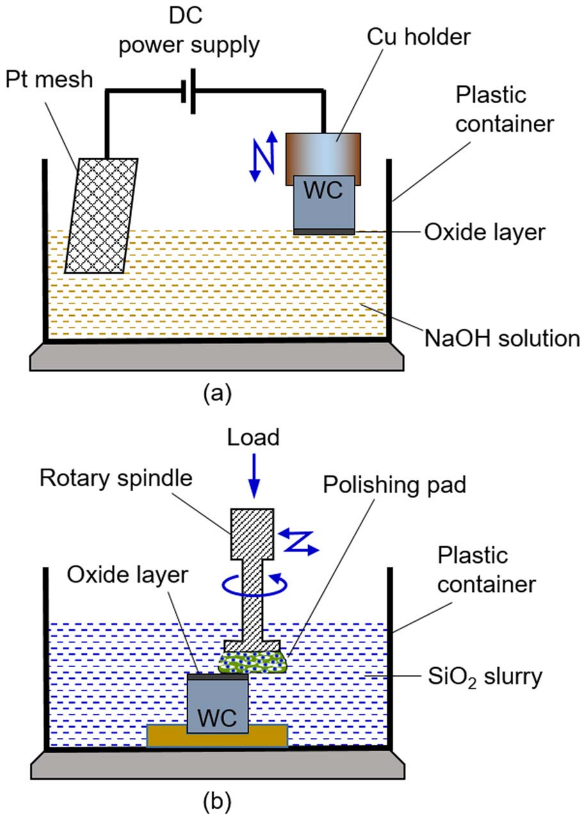


Figure 1. Schematics of experimental setups. (a) Anodizing setup. (b) Slurry polishing setup.

WC to investigate the surface anodizing (first step) and soft abrasive polishing (second step) characteristics and the results are reported in this paper.

Concept and Experimental

To realize the highly efficient and damage-free finishing of WC, ECMP, in which anodizing and abrasive polishing are simultaneously combined, is a promising approach. To confirm the applicability of ECMP to WC, there are several aspects need to be investigated including the anodizing behaviors of WC, the composition and hardness of the anodically oxidized layer, and the appropriate polishing conditions to remove the oxide layer and so forth. Thus, a two-step polishing process, in which anodizing and abrasive polishing are separately conducted, is proposed and experimentally studied in this work.

In the first step, anodizing of a diamond ground WC substrate was conducted to form an oxide layer. The WC substrates used in this research were supplied by Sumitomo Electric Industries and were consisted of WC grains (88%) and cobalt (Co) binder (12%). The substrates with a diameter of 10 mm were cut from a WC rod using electro-discharge machining and their end faces were ground using a diamond grinding wheel (#240). Figure 1a shows the schematic of the experimental setup used for anodizing. Anodizing was performed in a plastic container with electrolyte inside. Different types of electrolytes including potassium chloride (KCl), phosphoric acid (H_3PO_4) and sodium hydroxide (NaOH) solution with a weight concentration of 1.0% were used as the electrolytes for comparison. A platinum mesh (2 cm × 2 cm) was used as counter electrode and a WC substrate as working electrode. Keithley 2280S provided electric current to perform anodizing. To realize electric contact, the WC substrate was inserted into a copper holder which was mounted on a vertical lifting platform. Anodizing was conducted under a constant current mode ($I = 0.5$ A) so that the oxidized volume could be precisely controlled.

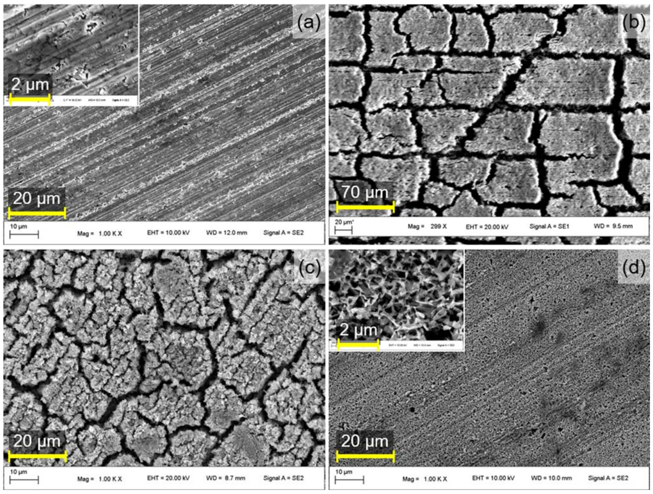


Figure 2. SEM images of WC surfaces. (a): the original as-ground WC surface; (b): anodized surface using KCl solution; (c): anodized surface using H_3PO_4 solution; (d): anodized surface using NaOH solution.

During anodizing, the position of the substrate was manually adjusted to ensure that only the downward end face was immersed in the electrolyte and oxidized.

It is assumed that WC grains will be oxidized to tungsten trioxide (WO_3) following Equation 1, while the Co binder will be oxidized to cobalt oxide (CoO) following Equation 2. Meanwhile, the oxidation products, WO_3 and CoO, are considered much softer than the original WC substrate so that polishing using soft abrasives can be realized.

$$2WC + 9O \rightarrow 2WO_3 + CO_2 + CO \qquad [1]$$

$$Co + O \rightarrow CoO \qquad [2]$$

In the second step, polishing using soft abrasives (SiO_2) was conducted to remove the soft oxide layer. Figure 1b shows the schematic of the polishing setup. Polishing was conducted in the same plastic container with SiO_2 slurry inside. Commercially available SiO_2 slurry (COMPOL 80) supplied by FUJIMI Incorporation was used in the polishing step. The initial SiO_2 weight concentration was 40% and was diluted to 10% by DI-water. The average diameter of SiO_2 powder in slurry was 72 nm. The WC substrate was fixed on the bottom of the container. A polishing pad with a diameter of 15 mm was pasted beneath the rotary spindle. The whole substrate surface was polished by reciprocating of the polishing tool which rotated with 10000 rpm. Two types of commercially available polishing pads, a hard non-woven type and a soft suede type, which were also supplied by FUJIMI Incorporation, were used for comparison.

As SiO_2 is much softer than WC, it is considered that only the soft oxide layer will be removed. Once the oxide layer is completely removed, the further material removal of WC by abrasion with SiO_2 abrasives can be neglected. Thus, the polishing step can be considered as a damage-free process without forming scratch and SSD. It is assumed that a flat and damage-free WC surface will be obtained after the oxide layer is removed by slurry polishing which will be experimentally investigated in this paper.

Results

Electrolyte selection for anodizing of WC.—As the first step of the proposed polishing approach, anodizing of WC was conducted. For electrolyte selection, KCl, H_3PO_4 and NaOH solutions were used for comparison. The anodizing duration was 5 min and the morphology of anodized surfaces were investigated using scanning electron microscopy (SEM). Figure 2a shows the SEM image of the as-ground WC surface. The surface was very rough and grinding marks can be

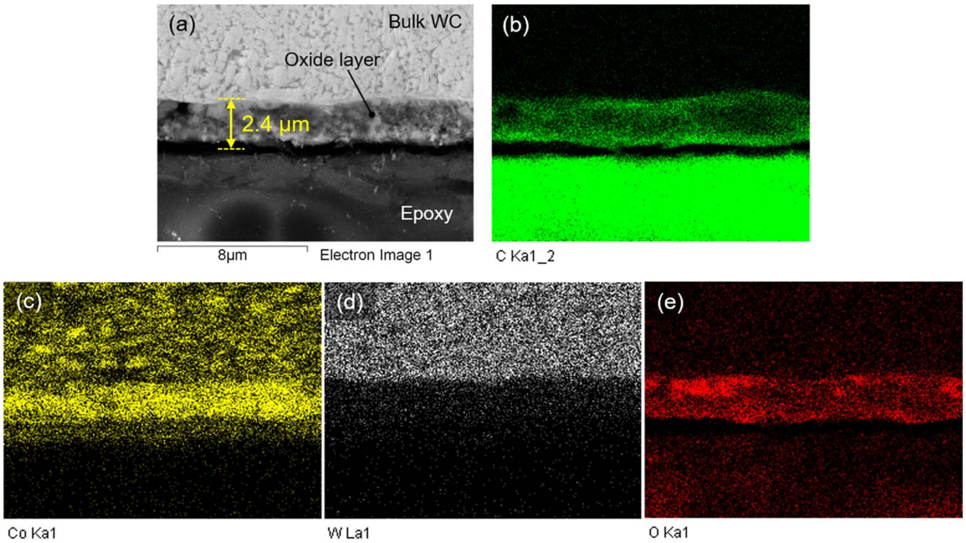


Figure 3. (a) Cross-sectional SEM image of the anodically oxidized WC surface (duration: 1 min); (b-e) EDX elemental mapping of the cross section.

clearly observed. When anodizing was conducted on the ground surface using KCl or H_3PO_4 as the electrolyte, surface morphology has greatly changed with the grinding marks completely eliminated, as shown in Figures 2b and 2c. Meanwhile, many cracks were formed. We found that the oxide layers shown in Figures 2b and 2c were non-dense and could be removed by wiping using soft papers. When NaOH was used as the electrolyte, the surface morphology as shown in Figure 2d was quite different with that using KCl or H_3PO_4. The oxidized surface was smooth and no crack was found. The insert in Figure 2d shows a high magnification SEM image of the oxidized surface. It was revealed that a porous oxide layer has been formed.

The probably mechanism to explain the above results is proposed. It has been reported that WO_3 can be dissolved in NaOH solutions while CoO can be dissolved in KCl and H_3PO_4. Therefore, in anodizing using KCl and H_3PO_4, the binding material cobalt was oxidized and dissolved by the electrolyte. Thus, the WO_3 grains which are oxidized from WC are separate and the oxide layer becomes nondense. Cracks were formed owing to the volume expansion when WC was oxidized to WO_3. On the other hand, for anodizing using NaOH, most of the WO_3 was dissolved by NaOH and CoO remained on the oxidized surface. This assumption can explain why the oxidized surface became porous.

In order to realize good surface roughness, it is required to form a dense but soft modified layer by removal of which a smooth surface can be obtained. In case of anodizing using NaOH, even though the WO_3 can be dissolved, the oxidized surface is denser than that formed by anodizing using KCl and H_3PO_4. Therefore, in following experiments, NaOH was used as the electrolyte for anodizing.

Anodizing of WC using NaOH.—In order to investigate the anodizing rate, the thickness of the oxide layer formed by anodizing using NaOH solution was measured using cross section SEM. Figure 3 shows the cross section SEM image of anodized WC with duration of 1 min as well as the Energy-dispersive X-ray spectroscopy (EDX) elemental mapping. It was found that an oxide layer with a thickness of about 2.4 μm was generated after anodizing for 1 min, demonstrating that anodizing of WC is a highly efficient modification process. In hybrid polishing combining material modification and mechanical removal, the MRR is usually limited by the surface modification efficiency especially for some chemically stable materials. In conventional finishing processes as previously introduced, their MRRs for WC are usually less than 30 nm/min.[21] Thus, it has been demonstrated that combination of anodizing and abrasive polishing is a highly efficient finishing process for WC owing to the high anodizing efficiency.

EDX elemental mapping results demonstrated that the main composition of the oxide layer is CoO and very little WO_3 was detected. Carbon was also detected in the oxide layer owing to the permeation from the epoxy layer. This result coincides with our assumption that the WO_3 can be dissolved by NaOH solution but the CoO layer will not be dissolved.

For further determination of surface composition, X-ray photoelectron microscopy (XPS) measurements were conducted before and after anodizing. As the detection depth for ceramics in XPS measurements is only several nanometers,[22] anodizing with a shortened duration of 2 s was conducted to generate a very thin oxide layer so that both the oxide layer and the bulk WC could be detected by XPS. Three locations on each sample were measured to exclude the location dependency and the measuring area was 0.9 μm in diameter. Figure 4 shows the W4f and Co2p spectra measured from the original WC surface and the anodized WC surface with an anodizing duration of only 2 s. All spectra were charge compensated to C1s at 284.8 eV corresponding to carbon contaminations.[23] On the as-ground WC surface, very weak peaks corresponding to Co-O bonds[24] were detected, demonstrating that a very thin CoO layer was formed which was considered owing to the native oxidation of Co binder. After anodizing, as shown in Figure 4b, peaks corresponding to WO_3[25] were newly detected with a strong intensity. Meanwhile, Co binder was almost completely oxidized within the XPS detection depth as shown in the Co2p spectra, which is considered owing to the lower oxidation potential of Co. The XPS results demonstrate that both WC grains and Co binder can be anodically oxidized as assumed. For the Co in WC substrate, besides CoO, $Co(OH)_2$, which was considered as the reaction product between CoO and NaOH solution was also detected by XPS as shown in Figure 4b.

An important precondition for the combination of anodizing and soft abrasive polishing is that the oxide layer must be significantly softer than the bulk substrate. Otherwise soft abrasive polishing cannot be applied and damage-free finishing cannot be realized. Thus, the difference of surface hardness before and after anodizing was investigated using a nano-indenter. 10 locations were measured for each sample and the maximum loading depth was set to 0.5 μm in both cases. Figure 5a shows the load-displacement curves obtained in nano-indentation tests on the original WC surface and the oxidized WC surface with an anodizing duration of 1 min. For the original WC surface, a maximum load of about 80 mN was required to reach the maximum loading depth while that for the anodically oxidized surface was only 13 mN, indicating that the oxidized surface was much softer than the original WC surface. As shown in Figure 3a, the thickness of the oxide layer after anodizing for 1 min (2.4 μm)

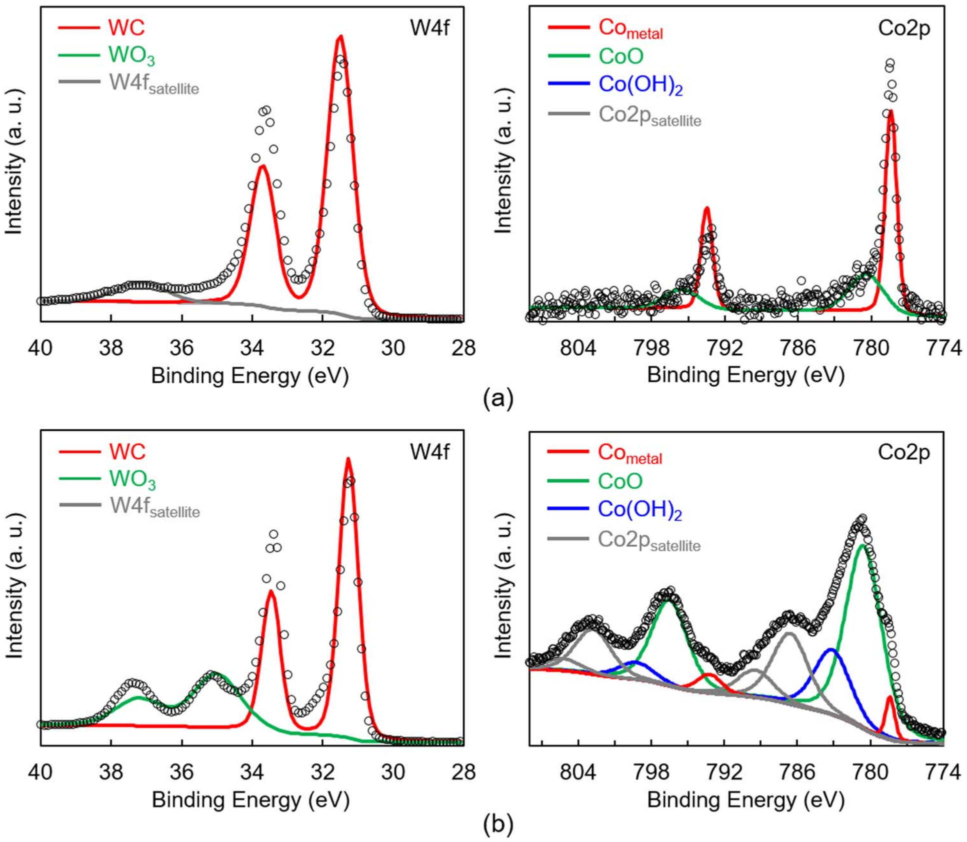


Figure 4. W4f and Co2p spectra of WC surfaces. (a) The original as-ground WC surface. (b) The anodically oxidized WC surface (duration: 2 s).

was much larger than the maximum loading depth (0.5 μm), ensuring that the measured hardnesses of the oxide layer was less affected by the bulk WC. Figure 5b shows the hardness of the original WC and oxidized WC with different duration increased from 1 min to 10 min. The hardnesses were calculated from the load-displacement curves measured by the nano-indenter. After anodizing, the surface hardness greatly decreased from 22.1 GPa to below 2.0 GPa, making it possible for the oxidized surface to be polished using soft abrasives.

Polishing of anodized WC.—The section above has experimentally proved that WC is able to be anodically oxidized and the oxidized surface is much softer than the original substrate surface. In this section, polishing of the oxidized WC surface using SiO_2 slurry was conducted to realize surface finishing.

Two types of polishing pads, a non-woven type and a suede type, were used for comparison. Figure 6 shows the SEM images of the pad surfaces. The pore ratio of the non-woven type polishing pad is much lower than that of the suede type polishing pad. According to

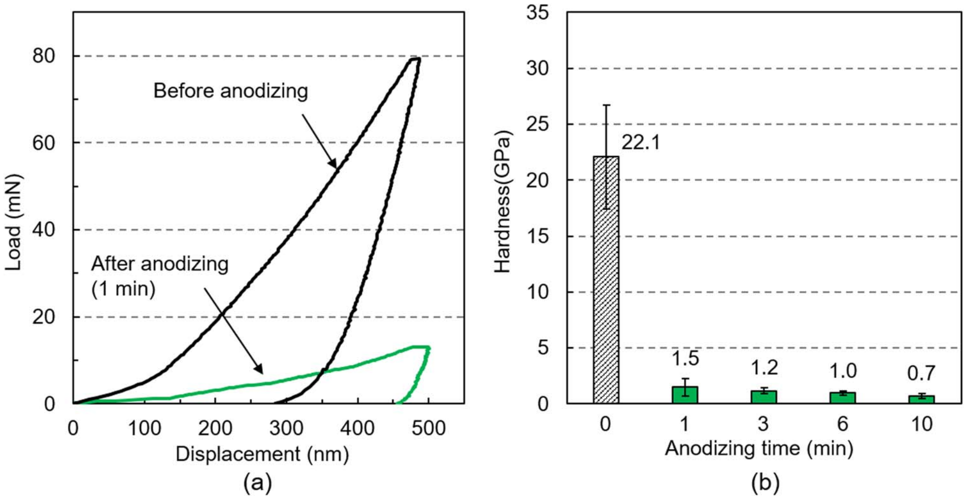


Figure 5. Nanoindentation tests on the as-ground WC surface and the anodized WC surface. (a) Load-displacement curves. (b) Hardness calculated from the load-displacement curves.

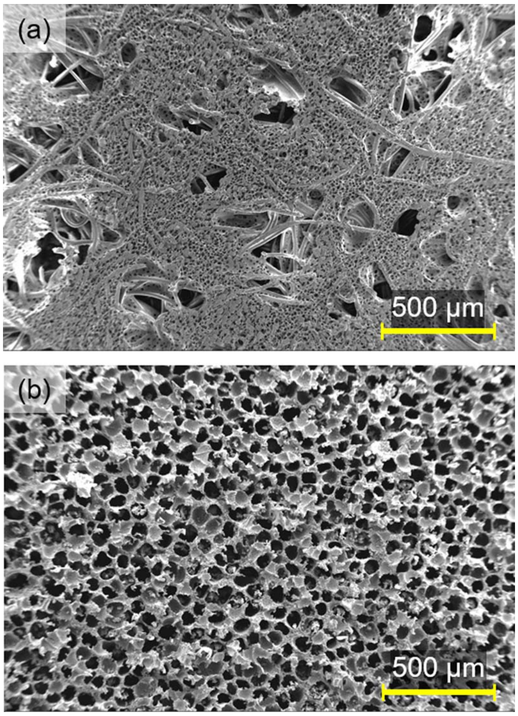


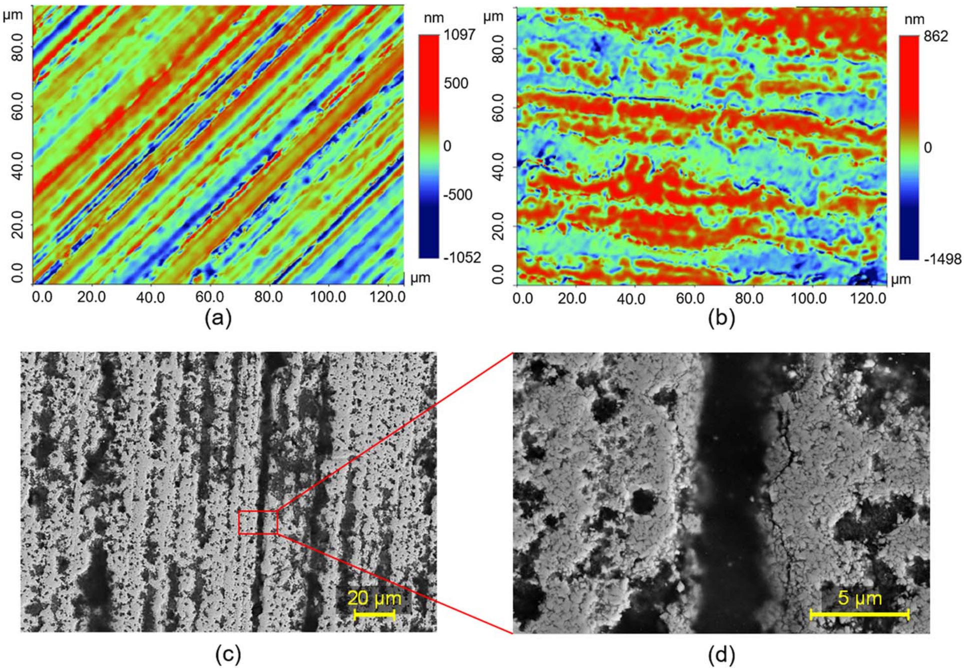
Figure 6. SEM images of the polishing pads. (a) The non-woven type polishing pad. (b) The suede type polishing pad.

specification, the non-woven type polishing pad (Shore-A hardness: 64°), which has been widely used for rough polishing, is much harder than the suede type polishing pad (Shore-A hardness: 43°) which has been widely used for final polishing. Thus, since the non-woven type polishing pad has more contact points and a higher hardness, its MRR also should be higher than that of the suede type pad.[26] As there was no reference for pad selection in slurry polishing of WC, the non-woven type and the suede type polishing pads were both used in the polishing step.

30 min of SiO_2 slurry polishing using a non-woven type polishing pad was conducted on an oxidized WC surface with an anodizing duration of 2 min. Figure 7a and 7b show the scanning white light interferometer (SWLI) images of the WC surfaces before and after polishing. It was found that the polished substrate surface was even much rougher than the original as-ground surface. The grinding marks disappeared while some nonuniform and wide grooves, which deteriorated the surface roughness, were observed after polishing. Observation of the polished surface within a larger observation scale was also conducted using SEM and the result is shown in Figure 7c. Compared with the morphology of the as-ground surface, these grooves obviously originated from the grinding marks on the original surface which were broadened during polishing.

The mechanism of groove generation is considered to be related to the preferential oxidation of damaged sites on the original WC surface. There is more residual stress and a deeper SSD layer around the grinding marks.[27] When anodizing is conducted on a damaged surface, the stress-rich sites like grinding marks or scratched areas, which are more chemically instable, will be oxidized preferentially during anodizing especially in the initial anodizing stage during which the oxide layer is thin.[19] When WC was anodically oxidized with a short duration, the interface between the oxide layer and bulk WC was actually rough with waviness as shown in Figure 3a. Thus, after polishing was conducted to remove the oxide layer, more material removal occurred along with the grinding marks, which were preferentially oxidized in the anodizing step, resulting in the generation of deeper and wider grooves shown in Figure 7c. As 2 min of anodizing was not enough to realize a featureless finishing of WC, two-step ECMP with a longer anodizing duration was conducted.

To eliminate the influence from initial grinding marks and realize a better surface roughness, a longer anodizing duration for 10 min was conducted to form a thick oxide layer. Figures 8a and 8b shows the SWLI and SEM images of the oxidized substrate surface. The porous structure, which greatly deteriorated the surface roughness, can be clearly observed. As anodizing was conducted under the constant current mode, the oxidation depth was supposed to be linearly



(a) (b)

(c) (d)

Figure 7. (a) SWLI image of the original as-ground WC surface (Sz: 1.10 μm, Sa: 154 nm). (b) SWLI image of WC surface processed by 2 min of anodizing and 30 min of silica slurry polishing using a non-woven pad (Sz: 862 nm, Sa: 213 nm). (c) SEM image of the polished WC surface. (d) Enlarged SEM image of a groove on the polished WC surface.

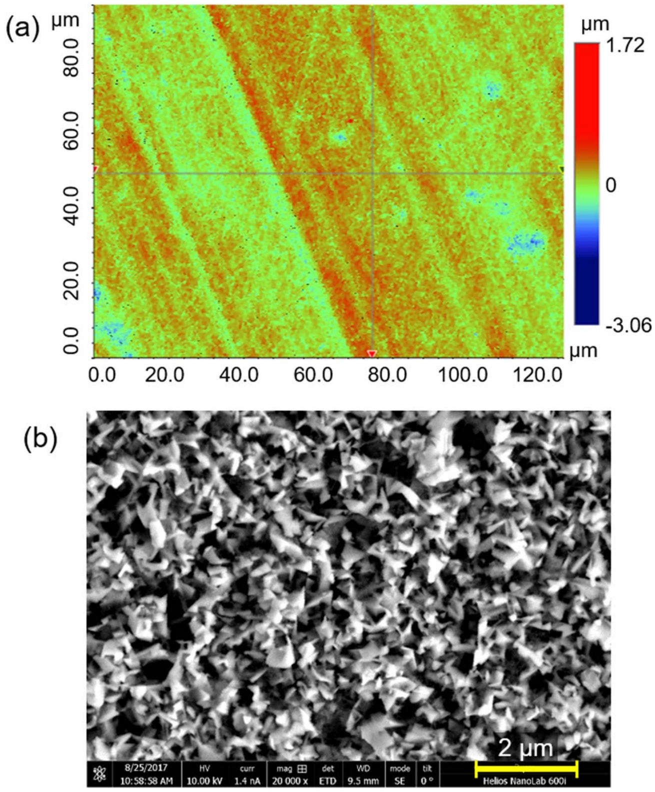


Figure 8. (a) SWLI image of the anodized WC surface with an anodizing duration of 10 min (Sz: 4.77 μm, Sa: 269.9 nm). (b) SEM image of the same surface.

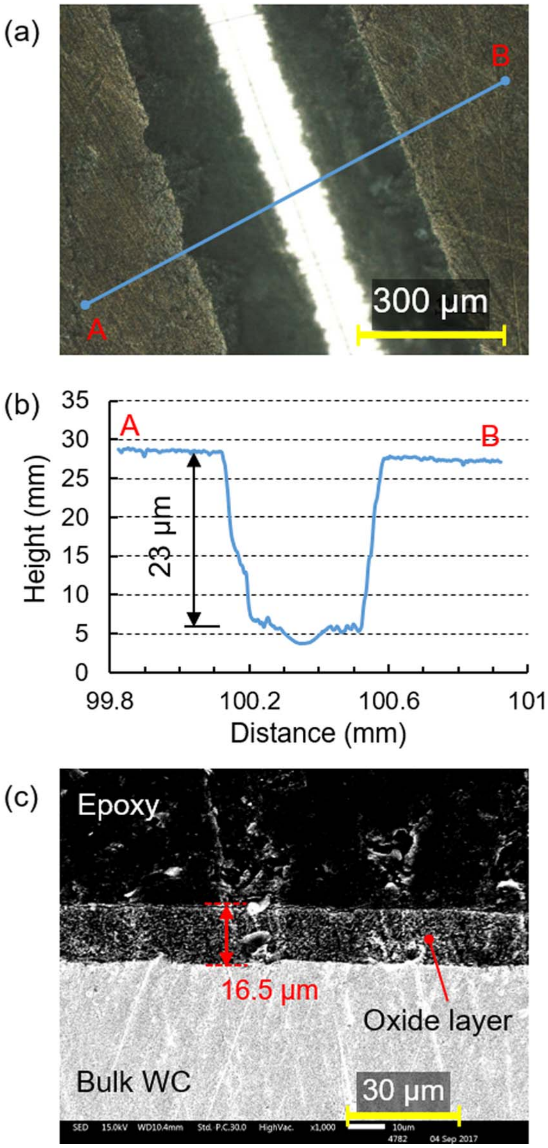


Figure 9. (a) Optical microscope image of the groove formed on the anodized WC surface. (b) Section profile of the groove. (c) Cross-sectional SEM image of the oxide layer (duration: 10 min).

dependent on the anodizing duration. Thus, according to Figure 3a, the oxide layer generated by anodizing of 10 min should be about 24 μm in thickness. In order to investigate the thickness of the oxide layer, a groove was formed on the anodized surface using a round-nose diamond cutting tool as shown in Figure 9a. Then, the section profile of the groove was measured using a stylus profilometer. As shown in Figure 9b, the central flat area is base WC with a high value of surface hardness, while the side area is the soft oxide layer which is relatively easy to cut with a low value of hardness by the diamond and has also been confirmed by SEM observation. The thickness of the oxide layer can be derived from the section profile to be about 23 μm, approximately 10 times of that of the oxide layer with anodizing duration of 1 min. This data supports our opinion that the oxidation depth is linearly dependent on the anodizing duration. Figure 9c shows the cross section SEM image of the oxide layer, whose thickness was measured to be only 16.5 μm. Such reduction of the thickness of the oxide layer was considered owing to the hydraulic compression (250 bar in this study) applied on the oxide layer, which is both soft and porous as shown in Figure 5 and Figure 8b, during the sample preparation process using a hot press mounting equipment (Struers Citopress-1) for cross section SEM observation.

Polishing of the oxidized surface using a non-woven polishing pad was conducted under the same conditions. Figure 10 shows the SWLI and SEM images of the polished surface. Compared with the original WC surface (Figure 7a) and the polished surface with a short anodizing duration (Figure 7b), the surface roughness was much better. The grinding marks were completely removed and grooves, which were generated when the anodizing duration was 2 min, were not observed. This result is in good agreement with the proposed groove generation mechanism. However, some scratches as well as some micro pits can still be observed on the polished surface. In this polishing experiment, the hard non-woven type polishing pad was used. Thus, horizontal collisions between the polishing pad and WC grains frequently occurred during polishing, resulting in the detachment of some WC grains. The detachment sites became larger during polishing and finally were transformed to micro pits as marked in Figure 10b. Such grain detachment phenomenon has been reported in machining of grain-based ceramics.[28] The detached WC grains, which are hard and brittle, then worked as the polishing media and introduced scratches on WC surface. Based on this mechanism, it is conclude that the hard non-woven type polishing is not suitable for ECMP finishing of WC and the soft suede type polishing pad is expected to achieve better performance.

Polishing of an oxidized WC surface using a suede type polishing pad was conducted under the same anodizing (10 min) and polishing (30 min) conditions. Figure 11 shows the SWLI and SEM images of the polished surface. The surface roughness, both Sz and Sa, are much smaller than these of the WC surface polished using a non-woven type polishing pad. As shown in Figure 11a, a smooth WC surface with a Sa roughness 55 nm has been obtained. As shown in Figure 11b, even though the SEM observation area is much larger than that shown in Figure 10b, scratch or micro pits were hardly seen. As the suede type polishing pad is relatively soft, the detachment of WC grains caused by mechanical collision during polishing has been suppressed. This result also supports the assumed mechanism of pit and scratch

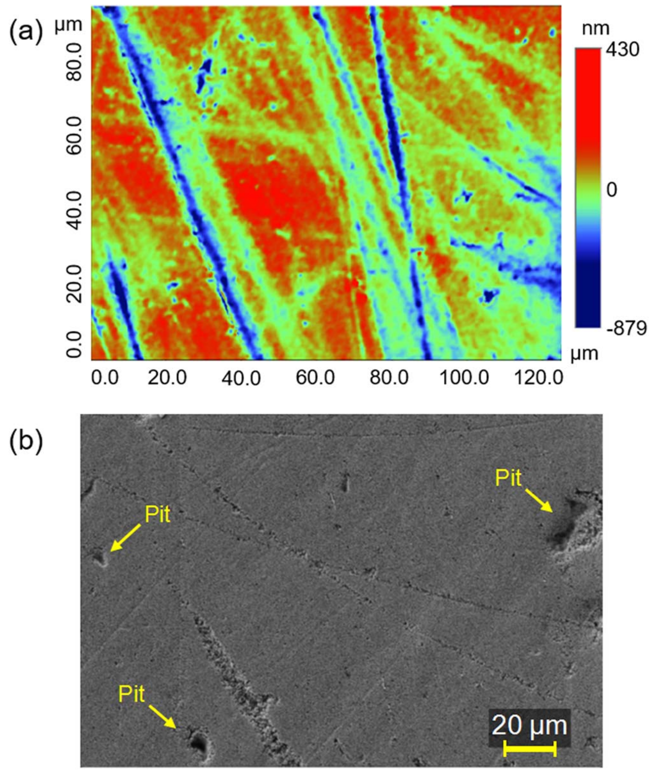


Figure 10. SWLI and SEM images of WC surface processed by 10 min of anodizing and 30 min of silica slurry polishing using a non-woven pad. (a) SWLI image (Sz: 430 nm, Sa: 83 nm). (b) SEM image.

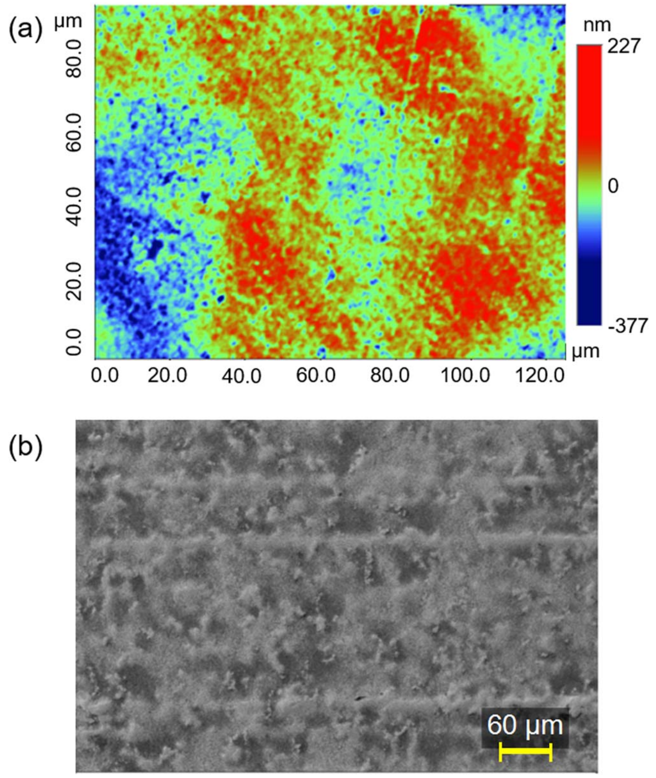


Figure 11. SWLI and SEM images of WC surface processed by 10 min of anodizing and 30 min of silica slurry polishing using a suede pad. (a) SWLI image (Sz: 227 nm, Sa: 55 nm). (b) SEM image.

generation in the two-step polishing process with a non-woven type polishing pad used.

From the application results, it has been proved that the combination of anodizing and soft abrasive polishing is an effective method to realize scratch-free finishing of WC. However, for glass lens molding, the achieved surface roughness 55 nm Sa is not good enough. There are two reasons why the polished surface was not as good as our previous work in which simultaneous ECMP was conducted to polish single crystal SiC.[19] First, the original surface ground by diamond wheel was two rough. Second, in the two-step polishing process described in this work, the oxide/WC interface can be considered as the finally achieved surface as further material removal hardly takes place once the oxide layer is completely removed. Therefore, there are still some waviness on the polished surface, which are considered originated from the oxide/WC interface generated by anodizing as can be observed from Figure 3a. It is expected that the WC surface can be further improved by using a simultaneously ECMP process, which will be validated in follow-up studies.

Conclusions

A two-step polishing process combining anodizing and soft abrasive polishing was developed to realize the damage-free and highly efficient finishing of WC. To summarize, the following conclusions can be drawn from this study:

1. WC can be anodically oxidized by using NaOH solution as electrolyte and the hardness of WC surface can be dramatically reduced by anodizing, making it possible to polish the modified surface using soft abrasives. Meanwhile, it has been proved that anodizing of WC is a highly efficient surface modification method compared with other modification methods used in other hybrid finishing processes.
2. The oxidized WC surface can be polished by SiO_2 slurry. The duration of anodizing and the type of polishing pad greatly affect the morphology of the polished WC surface. A scratch-free, pit-free and smooth WC surface with a Sa roughness of 55 nm can be obtained by combination of 10 min of anodizing and 30 min of slurry polishing using a suede type polishing pad.

This research offers a new method for achieving high-quality finishing of WC with high efficiency. As the applicability of combination of anodizing and soft abrasive polishing has been demonstrated by this work, the simultaneous ECMP, in which anodizing and soft abrasive polishing are simultaneously conducted, will be further studied in the future.

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