

## Electrochemical oxidation assisted ultra-precision optical microstructure machining on Tungsten Carbide superalloy

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### Abstract

Tungsten carbide (WC) superalloy has been widely used as an excellent mold material for its high hardness, good wear and corrosion resistance. However, the high hardness leads to the difficulty of machining optically qualified complex surfaces. Ultra-precision machining (UPM) technique uses crystalline diamond as a cutting tool, which enables the generation of optical surface in nanometre scale. Despite this, diamond cutting tool suffers both mechanical and chemical wear when cutting WC. In this study, an integrated method combining electrochemical oxidation and ultra-precision machining has been proposed. It is demonstrated that surface modification by electrochemical oxidation can drastically reduce the tool wear of the diamond tool. The surface morphology of the cross-section and surface composition were investigated. The results present that the material structure is modified and thus the hardness of the target area is effectively reduced, in turn extending diamond tool life.

Ultra-precision machining, tungsten carbide, electrochemical oxidation

### 1. Introduction

Tungsten carbide (WC) superalloy exhibits high toughness, good wear resistance and corrosion resistance and has been widely used for high-temperature applications, such as the mold material for precision glass molding (PGM) [1]. However, its high hardness makes it difficult to machine optically qualified surfaces. In addition, since the mold guarantees high surface quality and good shape accuracy of the optics, the efficiency of the PGM process highly depends on the molding tools [2]. Furthermore, to meet the sophisticated designs of devices, glass molding of complex features with the reduced size is required. Conventional grinding and polishing are incapable of generating complex freeform surfaces [3]. Therefore, recent research studies focus more on ultra-precision machining (UPM) of WC to achieve nanometric material removal with optical quality.

Diamond turning is deployed as an advanced technique that enables nano-level optical surface generation. Despite the high hardness of diamond cutting tools, mechanical and chemical wear are unavoidable when cutting tungsten carbide-cobalt (WC-Co) alloy. It is not economical to make optical glass mold through diamond turning [4]. To suppress the diamond tool wear in machining WC-Co, electrochemical oxidation (ECO) assisted diamond turning is proposed in this study. WC-Co alloy would be electrochemically oxidized (ECO-ed) in an alkaline environment and followed by the diamond turning process. The experimental investigation has been conducted.

### 2. ECO-assisted diamond turning process

ECO-assisted diamond turning process utilizes the coating nature of the anodizing process, the modified layer was softened so that the tool wear during the turning process can be minimized.

The experimental setup developed for this study is shown in Figure 1(a). It mainly consists of three parts: potentiostat, a Polytetrafluoroethylene (PTFE)-made electrolytic cell, and a personal computer (PC). The experimental data is captured by the PC software (Kickstart). During ECO, a WC90Co10 cemented superalloy workpiece was attached to the working electrode and pressed against an O-ring with an exposure area of  $\varnothing 10$  mm on the sidewall of the electrolytic cell. A platinum (Pt) mesh acts as the cathode. The experiment was conducted at a constant current of 0.5 A, with a varying exposure duration from 2 min to 120 min, for this study. NaOH solution with 1.0% weight percentage is used as electrolyte used in this study. ECO happens on the polished surface of WC-Co. It is found that non-adherent products would be formed on the ECO modified surface and the loose shell can be peeled off with ease. The following cutting test is performed after removing this "shell".

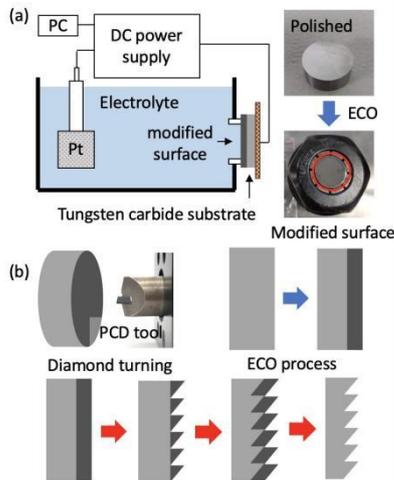
### 3. Experimental verification

To investigate more about the electrochemical reaction took place, scanning electron microscope (SEM), Energy Dispersive X-Ray Analysis (EDX) and X-ray photoelectron spectroscopy (XPS) were conducted to characterize the ECO modified surface and scratched surfaces. The underlying mechanism has also been analyzed based on the microstructure. The hardness was evaluated using a microhardness tester. The hardness of the WC-Co alloy reduced from 22 GPa to 3.4 GPa after ECO.

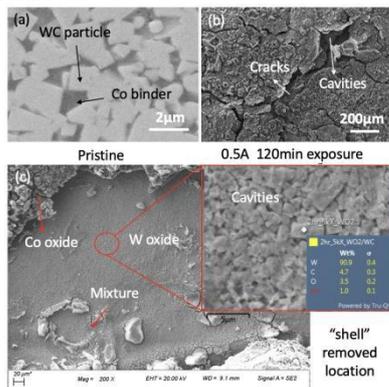
#### 3.1. SEM, EDX and XPS results

The SEM image of the WC-Co pristine surface is shown in Figure 2(a). After the 120min exposure of ECO under constant current 0.5A, it is observed that the surface is randomly distributed with cracks and cavities over the entire surface. With reference to the EDX results obtained, it is found that the Co element dominates the surface. This is due to the low activation

energy for Co. Compared with WC, Co is relatively more active, thus was oxidized with priority. The XPS results shows the coexistence of Co oxide and metallic Co, the valences are 2+ and 0, respectively. The trivalent Co cations are unstable and it is easily to be oxidized, and finally passive CoO form on the surface.



**Figure 1.** Schematic diagram of the ECO assisted diamond turning process (a) ECO process and (b) hybridized diamond turning of the modified surface.



**Figure 2.** SEM and EDX of the ECO modified surface of WC90Co10 (a) pristine; (b) after 120min @ 0.5A and (c) "Shell" peeled location exposing the WC underneath.

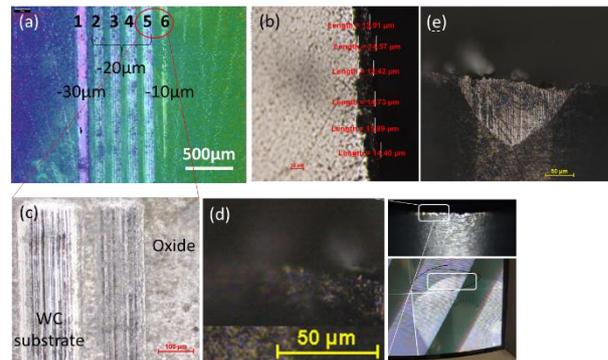
In addition, Tungsten oxide, especially  $WO_3$ , would dissolve in the alkaline electrolyte (even slowly in water), leading to its low content in the oxide layer. As the reaction proceeds, WC phase is also oxidized emitting  $CO_2$ , which breaks the loose structure of Co oxide. Furthermore, the non-adherent Co oxide, namely "shell" can be removed easily. Based on the

After the leach-out, the underlying tungsten oxide would appear on the surface, as shown in Figure 2(c). Based on the investigation, the exposed W oxide surface consists of WC,  $WO_2$  and  $WO_3$ , tungsten ions with different ionic valence coexist on the surface.

### 3.2. Machining test with PCD tools

To evaluate the machinability of the ECO layer, scratch test was conducted on the workpiece with the longest reaction time (120min @ 0.5A). The results are illustrated as in Figure 3. Six paths with different depth of cut were machined on the surface using a PCD tool. The depths of cut are defined as  $30\mu m$ ,  $20\mu m$  (2-5) and  $10\mu m$ , respectively. As in Figure 3(b), the maximum oxide layer thickness measured is  $15.89\mu m$ , showing that the modified ECO layer should be removed at the designed depth of cut. The oxide film distributes uniformly on the surface and the oxide film thickness does not show big discrepancy. The occurrence of oxidation reaction highly depends on the surface

activation energy locally, while in this case, the surface has been pre-polished and the surface condition is uniform. Therefore, uniform oxide layer has been observed, as shown in Figure 3(b). As shown in Figure 3(c), the WC substrate was exposed after the diamond tool completely removed the oxide layer during the machining. It is worthwhile to note that, the PCD tool does not show any wear after the 6 rounds of machining trials, as shown in Figure 3(d). On the contrary, Figure 3(e) shows a worn tool after directly machined on unprocessed WC-Co surface. Overall, Figure 3 shows a significant suppression of tool wear when machining the ECO layer instead of the original WC-Co material directly.



**Figure 3.** Scratch test by PCD tool (a) six scratches with different depth; (b) cross-section of the workpiece (0.5A, 120min exposure); (c) Enlarged scratch #5 and #6; (d) microscopic image of the PCD tool showing minimal tool wear and (e) tool wear of PCD after direct machining of the WC-Co alloy.

## 4. Results and discussion

During the ECO process, Co has the priority to be oxidized. The CoO oxide formed is loose and non-adherent and therefore can be easily peeled off due to the oxidation of the underlying WC and the dissolution of W oxide. Despite this, the material structure modification by the ECO process can effectively reduce surface hardness. The modified WC-Co surface can be removed directly by the PCD tool and no obvious tool wear was observed, due to both the hardness reduction and the metallic Cobalt and Tungsten, which will cause chemical erosion to the diamond.

## 5. Conclusion

In this study, ECO-assisted diamond turning has been conducted on a WC90Co10 cemented carbide. The mechanism of the ECO surface modification process has been illustrated. It is found that the hardness of the target area was reduced, despite the loose structure of the CoO. A scratch test by PCD tool was conducted and it is shown that the modified layer can be removed without the generation of tool wear. This provides a potential method that can increase diamond tool service life.

## References

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