Theoretical and experimental investigation of chemical mechanical polishing of W–Ni–Fe alloy

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Received 21 October 2020, revised 29 November 2020
Accepted for publication 16 March 2021
Published 6 April 2021

Abstract
Fine finishing of tungsten alloy is required to improve the surface quality of molds and precision instruments. Nevertheless, it is difficult to obtain high-quality surfaces as a result of grain boundary steps attributed to differences in properties of two-phase microstructures. This paper presents a theoretical and experimental investigation on chemical mechanical polishing of W–Ni–Fe alloy. The mechanism of the boundary step generation is illustrated and a model of grain boundary step formation is proposed. The mechanism reveals the effects of mechanical and chemical actions in both surface roughness and material removal. The model was verified by the experiments and the results show that appropriately balancing the mechanical and chemical effects restrains the generation of boundary steps and leads to a fine surface quality with a high removal rate by citric acid-based slurry.

Keywords: chemical mechanical polishing, W–Ni–Fe alloy, grain boundary step, modelling, mechanism

Nomenclature

| Symbol | Description |
|--------|-------------|
| C      | ratio of the total polishing pressure to the polishing pressure on the designated region |
| h      | height between the polishing pad and workpiece |
| K      | ratio of the actual saturated grain boundary step to the theoretical saturated grain boundary step |
| $K_M$  | ratio of the matrix phase hardness of the reaction layer to the hardness of the matrix phase |
| $K_W$  | ratio of the tungsten phase hardness of the reaction layer to the hardness of the tungsten phase |
| $t_M$  | reaction layer thickness of the matrix phase |
| $t_W$  | reaction layer thickness of the tungsten phase |
| $v$    | velocity of an individual abrasive |
| $A_0$  | nominal contact area between the pad and workpiece |
| $A_1$  | real contact area between the polishing pad and workpiece |
| C      | shape constant |
| $D$    | diameter of an abrasive |
| $E'$   | elastic modulus of the polishing pad |
| $F'$   | polishing pressure acting on the designated region |

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contact force of the abrasive and workpiece
contact force between the abrasive and polishing pad
hardness of the workpiece
number of effective abrasives
nominal contact polishing pressure between the workpiece and polishing pad
real contact polishing pressure between the workpiece and polishing pad
abrasive volume concentration of the polishing slurry
radius of circular indentation on the workpiece surface by an abrasive
ratio of the actual material removal volume to the theoretical material removal volume
indentation depth of abrasives into the polishing pad
indentation depth of abrasives into the matrix phase
indentation depth of abrasives into the matrix phase at saturation
indentation depth of abrasives into the tungsten phase
indentation depth of abrasives into the tungsten phase at saturation
contact ratio
density of asperity
poisson ratio of the polishing pad
standard deviation of the asperity height distribution
depth of the grain boundary step
cross-sectional area of the deformed area on the workpiece
reduce the production of cutting heat due to the high hardness and strength of tungsten particles in cutting tungsten alloys, resulting in grievous tool wear and low machining efficiency [14]. The experimental results indicated that the material removal rate (MRR) was three times higher than that of traditional coolants, and the cutting force and surface roughness were reduced by 30% and 20%, respectively. The final surface roughness (Ra) reached Ra = 1.5 nm. In order to avoid tool adhesion and brittle and fast wear in tungsten alloy processing, Suzuki et al utilized elliptical vibration cutting with a single crystal diamond cutter to process a tungsten alloy mold [15]. They reported that the surface roughness of the prism surface was Rz = 40 nm, and the surface roughness of the spherical lens was Rz = 100 nm. Nevertheless, the surface quality obtained by the above processing technology cannot fully meet the requirements of the mold, and there are still some defects, such as knife marks and cracks on the surface. Chemical mechanical polishing (CMP) plays a vital role in precision/ultra-precision machining and has been widely used for finishing glass, semiconductor Si wafers and other materials due to its global flattening capability [16–19]. In CMP, chemical-mechanical synergy (CMS) has a significant influence on material removal (MR) and has been comprehensively studied. In general, there appear to be three main approaches for investigating CMS effects and establishing corresponding quantitative models. The first approach is to introduce chemical action on the basis of mechanical action. Chemical action was attributed to dynamic hardness changes [20–23]. The second approach is to introduce surface reaction kinetics into the MR model based on mechanical-assisted chemical effects and diffusion theory [24–26]. According to the removal mechanism of the molecular scale, the third approach is to describe CMS as an alternation of bonded molecular species formation and removal [27, 28]. However, the above CMS models are described for monocrystals or single-phase materials and cannot characterize the process of polycrystalline or multiphase materials due to the discrepancy of material properties between different phases.

Notably, W–Ni–Fe alloy is a typical multiphase material, however it is difficult to obtain supersmooth surfaces from multiphase and polycrystalline materials due to the physical and chemical differences in phase and orientation [29, 30]. The reason lies in the grain boundary step that tungsten alloys, and polycrystalline materials, produce in the traditional CMP process, which worsens the surface roughness in processing. In order to obtain a supersmooth surface of the YAG polycrystalline ceramic, Suzuki et al developed a mixed polishing slurry nanodiamond and colloidal silica. The results showed that grain boundary steps were effectively suppressed, and the surface quality was improved at an appropriate ratio of nanodiamond and colloidal silica, obtaining minimum surface roughness \( R_z = 3.85 \text{ nm}, \ Ra = 0.56 \text{ nm} \) [15]. However, up to now, limited work has been reported on the CMP of multiphase materials, such as tungsten heavy alloys.

In this paper, CMP was selected as the final process to improve surface quality and increase removal rates. However,
as shown in figure 1, a grain boundary step formed due to different hardness between the tungsten phase and the matrix phase, which primarily contains nickel (Ni), iron (Fe) and tungsten (W). As a result, it is difficult for traditional CMP to achieve an ultra-smooth surface. In addition, similar phenomena have also been observed in polycrystalline materials. This paper studies the mechanism of grain boundary step generation in CMP of W–Ni–Fe alloy. The objectives of the study are (a) to present a qualitative understanding of the grain boundary step evolution mechanism and establish a general evolution model suitable for polycrystalline and multi-phase materials of grain boundary steps; (b) to discern the effects of the mechanical and chemical actions of the CMP process in MR generation of surface roughness and MR to minimize grain boundary steps; (c) to study the influence of CMP process parameters such as polishing pressure, abrasive size and abrasive concentration on grain boundary steps, and to verify the model.

2. Mechanism of boundary step generation

The mechanism of grain boundary step formation can be explained in figure 2. Due to the presence of chemical substances in the polishing slurry, a thin reaction layer formed on the surfaces of both the tungsten phase and matrix phase. This reaction layer can be removed more easily than the substrate material. With the removal of micro-scratches, the surface became smooth and the roughness value reached the inflection point. Then, due to the different hardness of the reaction layer between the tungsten phase and matrix phase, based on the micro-contact mechanism, the indentation depths of particles on the two phases differed when applying the same pressure on them, which resulted in different mechanical MR. This led to different MRR on the two phases, resulting in the formation of grain boundary steps. Under conditions of $\delta_w = \delta_m$, the grain boundary steps reached a saturation state, which is affected by abrasive particle size, pressure, chemical reaction, etc. Accordingly, the surface roughness tends to be stable.

3. Modelling

When polishing with free abrasives, the polishing slurry containing abrasives flows between the workpiece and polishing pad. Some of the abrasives are located in the grooves of the polishing pad do not come into contact with the workpiece surface, so their MR effect on workpiece is negligible. Another portion of abrasives is located on the micro convex peak of the polishing pad and then embedded into them under the effect of load. With the relative movement between them, part of the abrasives is dragged across the workpiece surface to remove the material. Therefore, this paper only studies the MR process of those effective abrasives. In this model, the polishing process is simplified, and the following assumptions are made.

The abrasive particles are spherical rigid bodies of SiO$_2$ with the same size, and the deformation of the abrasives is ignored. The abrasives are evenly distributed in the polishing slurry, and the number of effective abrasives acting on the tungsten phase is same for the matrix phase per unit.

The parameters in this model are shown in table 1.

3.1. Polishing pad in contact with workpiece

The micro-contacts between the polishing pad and the workpiece surfaces can be modelled by the classical Greenwood and Williamson (GW) elastic model [35]. According to the GW model, the contact ratio $\varepsilon$ can be expressed as:

$$\varepsilon = \frac{A_t}{A_0} = \pi \eta R \int_{D_0}^{+\infty} (z - D) \varphi(z) \, dz. \quad (1)$$

The nominal contact polishing pressure between them can be expressed as:

$$P = \frac{4}{3} \eta E^* R^2 \int_{D_0}^{+\infty} (z - D)^2 \varphi(z) \, dz \quad (2)$$

where \( \varphi(z) = \exp(\frac{-z^2}{2\omega^2})/\omega \sqrt{2\pi} \), $\omega$ stands for the standard deviation of the asperity height distribution, $A_0$ stands for the nominal contact area between the pad and workpiece. $A_t$ stands for the real contact area between the polishing pad and workpiece. $\eta$ stands for the density of asperity. $R$ stands for the radius of the pad asperity summit, and $z$ stands for the height of asperity. $D$ stands for the diameter of abrasive. Since the pad is usually much softer than the W–Ni–Fe alloy, the composite modulus between the pad and workpiece can be described as $E^* = E_p/(1-v_p^2)$ where $E_p$ and $v_p$ are the Young’s modulus and the Poisson’s ratio of the pad, respectively.

Thus, the relationship between $P$ and $P_t$ can be indicated as:

$$PA_0 = P_t A_t. \quad (3)$$

To obtain an explicit form, the ratio of equations (1) and (2) could be approximated as a constant [36].
Figure 2. Mechanism of grain boundary steps formation.

Table 1. Material mechanical properties [31–34].

| Properties           | Tungsten phase | Matrix phase | Polishing pad |
|----------------------|----------------|--------------|---------------|
| Hardness (GPa)       | 5.5            | 5.5          | 0.009         |
| Elastic modulus (GPa)| 280            | 170          | 0.025         |
| Poisson ratio        | 0.3            | 0.3          | 0.2           |
| Mean contact pressure factor | 0.4           | 0.4          | 0.4           |

\[ A_t = CA_0 \left( \frac{R}{\omega} \right)^{\frac{1}{2}} \left( \frac{P}{E^*} \right)^{\frac{1}{2}} \]  

where \( C \) is a shape constant whose value is related to the shape of the groove on the surface of the polishing pad.

From equations (3) and (4), \( P_t \) is given as:

\[ P_t = \frac{E^*}{C \varepsilon^2 \left( \frac{\omega}{R} \right)^{\frac{1}{2}}} \]  

3.2. Analysis of polishing pad-abrasives micro-contact states

The penetration depth of an abrasive can be compared in two phases that incorporate the analysis of the abrasive’s force equilibrium. In this study, elastic deformation, rather than plastic deformation, is assumed at the pad/abrasive contact interface. Figure 3 shows the scanning electron microscope (SEM) (NOVA NanoSEM, FEI, USA) imaging of the polishing pad-abrasives’ micro-contact after polishing. Since the polishing pad is non-conductive, the workpiece was sprayed with gold before being shot. Figure 3(a) reveals the surface of the polishing pad as a porous structure with a diameter of 20–40 \( \mu \)m. In addition, the abrasives adhered to the surface of the polishing pad and no obvious embedding phenomenon was observed, as shown in figure 3(b), which proves that the pad-abrasives contact interface is elastic deformed. Moreover, the contact interface between the workpiece and abrasive is assumed to be plastic deformed [23, 37]. The method of calculating the contact force between the abrasives and polishing pad/workpiece can be obtained according to their contact form.

As shown in figure 4(a), the elastic contact force between the abrasives and polishing pad \( F_p \) can be described as [36]:

\[ F_p = \frac{4}{3} E^* \left( \frac{D^2}{2} \right)^{\frac{3}{2}} \]  

where \( \delta_p \) is the indentation depth of the abrasives into the polishing pad. Furthermore, the plastic contact force \( F_a \) between them can be described as:

\[ F_a = \pi a^2 H^* \]  

where \( a \) is the radius of circular indentation on the workpiece surface by the abrasives, as illustrated in figure 4. \( H^* \) is the hardness of the workpiece.

There is a geometric relationship between \( a \) and the critical contact interference of the workpiece

\[ a^2 = \left( \frac{D}{2} \right)^2 - \left( \frac{D}{2} - \delta_a \right)^2 \]

\[ = D \delta_a - \delta_a^2 \approx D \delta_a. \]  

In addition, the indentation depth of abrasives into the polishing pad \( \delta_p \), critical contact interference of the workpiece \( \delta_a \), and diameter of the abrasives \( D \) satisfies the following geometric relationship:

\[ \delta_a + \delta_p = D. \]  

Combining equations (6)–(9) provides the values: \( \delta_p, \delta_a \). In the CMP process, a soft reaction layer forms on the surface of the W–Ni–Fe alloy. Thus, it is necessary to analyze the
thickness of the reaction layer because its material properties differ from those of the substrate material and affect the depth of the abrasive indented into the W–Ni–Fe alloy. Qin et al [23] quantified the influence reaction layer thickness on the MRR and reported that the thickness of oxide reaction layer ranges between 0.5 and 1 nm. By substituting the parameters of the W–Ni–Fe alloy into equations (5)–(8), the estimated indentation depth of abrasives into W–Ni–Fe is around 0.1 nm, which is less than the thickness of the reaction layer, as illustrated in figure 4.

Considering the linear proportional relationship between the hardness of the reaction layer and workpiece:

\[ H_{W1} = k_W H_W \]  \hspace{1cm} (10)

\[ H_{M1} = k_M H_M \]  \hspace{1cm} (11)

where \( H_W \) is the hardness of the tungsten phase, \( k_W \) is the ratio of the hardness of reaction layer to the hardness of the tungsten phase. Script ‘W’ and ‘M’ represent tungsten phase and matrix phase, respectively. It is assumed that the hardness changes of the two phases are nearly equal, namely \( k_W \approx k_M \).

The force equilibrium of an individual abrasive is:

\[ F_p = F_a \]  \hspace{1cm} (12)

Therefore, the relationship between \( \delta_p \) and \( \delta_a \) can be obtained by substituting equations (6)–(8) and (10), into equation (12)

\[ \delta_p = \left( \frac{3\sqrt{2}\pi k_W H^* D^2}{4E^*} \delta_a \right)^{\frac{2}{3}}. \]  \hspace{1cm} (13)

As illustrated in figure 4(a), the surface of the W–Ni–Fe alloy has not yet formed a height difference between two phases that

\[ h_W = h_M \]  \hspace{1cm} (14)

\[ \delta_W + \delta_{pW} = \delta_M + \delta_{pM}. \]  \hspace{1cm} (15)

Substituting equation (13) into equation (15) with the parameters of the tungsten and matrix phases yields:

\[ \delta_W + 329k_W \delta_{W}^{\frac{2}{3}} = \delta_M + 288k_W \delta_{M}^{\frac{2}{3}}. \]  \hspace{1cm} (16)

Because the hardness of matrix phase is less than that of tungsten phase, it can be deducted from equation (16) that:

\[ \delta_M > \delta_W, \delta_M > 0, \delta_W > 0. \]  \hspace{1cm} (17)

### 3.3. MRR

The cross section of the deformed area of the workpiece due to the embedding of abrasives \( \Delta s \) is approximately given by [34]:

\[ y = \frac{3\sqrt{2}\pi k_W H^* D^2}{4E^*} \delta_a \]
\[ \Delta s = \delta_a \sqrt{\frac{p_a D}{\pi}}. \]  
(18)

The MRR of the workpiece is obtained by:
\[ \text{MRR} = \beta \cdot \Delta s \cdot v \cdot N_a = \beta \cdot v \cdot N_a \cdot \delta_a \sqrt{\frac{p_a D}{\pi}} \]  
(19)

where \( \beta \) is the ratio of the actual MRR volume to the theoretical MR volume, \( v \) is the velocity of an individual abrasive, \( N_a \) stands for the number of effective abrasives.

Since the uniformity of the processing is considered, all the parameter values in equation (19) are the same, except for \( \delta_a \). Therefore, the MRR of the tungsten phase is greater than that of the matrix phase, according to \( \delta_M > \delta_W \).

This difference in MRR results in the MR depth of the matrix phase being larger than that of the tungsten phase during the same polishing time. As a result, the matrix phase is shorter than the tungsten phase after polishing. The height difference form between two phases. Hence, it can be explained that the hardness difference between these two phases is the fundamental reason for the formation of grain boundary step topography.

3.4. Saturated grain boundary step

As the polishing time increases, the MR depth gradually increases. At the same time, due to the different MRRs of the two phases, the grain boundary step depth (equal to the height difference between two phases) gradually increases, which can be regarded as the boundary steps of the matrix phase gradually becoming bigger. This phenomenon weakens the removal effect of abrasives on the matrix phase, so the MRR of the matrix phase gradually decreases. The speed of the grain boundary step depth gradually slows down. When the two phase reach the same MRR, the grain boundary step depth reaches the saturated state and does not change any more.

Since the MR depth of an individual abrasive can reflect the MR depth of the workpiece, an approximate slurry of the saturated state and does not change any more. The number of effective abrasives in MR can be calculated as [33]:
\[ N_a = A(\frac{6V_c}{\pi D^3})^{\frac{3}{2}} \]  
(23)

where \( V_c \) is the abrasive volume concentration in the polishing slurry. Then, \( \delta'_W \) and \( \delta'_M \) can be calculated by using equations (7)–(22):
\[ \delta'_W = \delta'_M = \frac{cF}{\pi N_a \delta_W (H_W + H_M)}. \]  
(24)

So the \( \delta'_pW \) and \( \delta'_pM \) can be obtained from equation (13):
\[ \delta'_pW = \left[ \frac{3\sqrt{2}\pi c F H_W}{4E' N_a D^2 (H_W + H_M)} \right]^{\frac{3}{2}} \]  
(25)
\[ \delta'_pM = \left[ \frac{3\sqrt{2}\pi c F H_M}{4E' N_a D^2 (H_W + H_M)} \right]^{\frac{3}{2}}. \]  
(26)

Therefore, the saturated grain boundary step \( \Delta \) can be obtained by substituting equations (3)–(26) into equation (20):
\[ \Delta = K \left[ \frac{\omega^2 p^4 D^2}{V_c^2 R^2 E^2 (H_W + H_M)} \right]^{\frac{3}{2}} (H_W^{\frac{3}{2}} - H_W^{\frac{3}{2}}) \]  
(27)

where \( K = \frac{3k}{2\sqrt{3}} \left( \frac{\pi c}{6C} \right)^{\frac{3}{2}} \).

In summary, the verification of the grain boundary step model in this paper was divided into two steps. Firstly, reasonable experimental parameters were designed and the actual grain boundary step was measured to calibrate \( K \). Secondly, the model was verified by experimental parameters including polishing pressure, abrasive size and abrasive concentration.

4. Experimental setup and conditions

The material used in this experiment was a 95W–3.5Ni–1.5Fe alloy, which was prepared through liquid phase sintering of W, Ni and Fe mixed powder. Detailed material information can be found in [31]. The sample was a cylinder with a 15 mm diameter and 7 mm height. The pretreatment process of the workpiece involved grinding the sample with an 80 grit-sized diamond grinding wheel and 38 nm, 25 nm, 18 nm and 15 nm silicon carbide abrasives, respectively. The sample was ground with a fixed diamond grinding pad with a particle size of about 5–10 nm.

Figure 5 shows the experimental setup for the CMP. Three workpieces spaced at an interval of 120° were bonded to the sample tray with paraffin. An IC 1000/Suba IV polishing pad (Rohm & Hass Inc.) was used as the polishing pad due to its uniformity. The experimental conditions are listed in table 2. SiO₂ hydrosol (COMPOL, FUJIMI Corporation) was adopted as a free abrasive due to its stability, dispersity and moderate hardness. It leaves fewer surface scratches than other...
abrasives. The average particle size of the silica in the hydrosol was 70 nm. The abrasive concentration was chosen as 15 wt%, and the flow rate of polishing slurry was set at 4.5 ml min$^{-1}$. In order to study the influence of chemistry on polishing, three pH levels of the polishing slurry were selected: an alkaline-based slurry, with an original pH of 10, was mixed with citric acid to produce two slurries with pH values of 7 and 4, respectively.

5. Results and discussions

5.1. Surface topographies

As illustrated in figure 6, the surface topographies of 95W–3.5Ni–1.5Fe alloy by different lapping and polishing conditions were observed by a metallurgical microscope (MX40, Olympus). Figure 6 shows that using smaller abrasive particles during the lapping process resulted in shallower scratches. In addition, figures 6(e) and (f) demonstrate that the workpiece surface became smoother after processing it with a diamond fixed abrasive pad. The defects and scratches caused by lapping gradually became smaller and eventually disappeared as the polishing time increased. At the same time, the grain boundary gap that formed between the tungsten phase and the matrix phase gradually became deeper, resulting in a grain boundary step topography on the surface of the W–Ni–Fe alloy. This topography may have occurred as a result of the different MRRs of the two phases due to the difference of hardness. In addition, in order to study the chemical effect of the slurry on surface topography, two tests were conducted using acidic and alkaline polishing slurries. The grain boundary step topography was more obvious in the alkaline environment.

5.2. Surface roughness and MRR by lapping

The surface roughness of the W–Ni–Fe alloy was measured by an optical interferometry profiler (NV5000 5022S, ZYGO) with a vertical resolution of 0.1 nm. Nine points were selected on the workpieces as measuring positions, and the results are shown in figure 7. At the lapping stage, the surface roughness of workpiece decreased as the particle size decreased. This is because the depth of the abrasive particles penetrating...
into the workpiece material is related to the size of the abrasive particles. Under the same experimental conditions, smaller particles have shallower penetrating depths, resulting in shallower scratches on the workpiece surface due to the mechanical effect of the abrasive particles. Meanwhile, due to the uneven distribution of particle sizes, the actual abrasive particle size is distributed in a range. The average value of the abrasive particles was chosen to represent the size of the abrasive particles. In addition, the measurement result of the MRR is shown in figure 8. The measurement details of MRR are illustrated in the appendix. The MRR during the lapping period decreases with the as the abrasive particle size decreases.

5.3 Surface roughness and MRR by polishing

Surface roughness and MRR were both measured periodically during the polishing. The optical interferometry profiler (NV5000 5022S, ZYGO) was used to measure the surface roughness. The surface roughness results are shown in figure 9. In general, the surface roughness appears to drop rapidly first under different pressures and then reaches a minimum point, and finally reaches a steady state value over a period of time.

Figure 10 shows an example of the 3D surface topography of the workpiece at pH = 10.5 under different polishing stages. The surface roughness reaches a minimum at the inflection point. In the initial state (i.e. before polishing), the surface of the workpiece is covered with tiny scratches left by the grinding. When the polishing process reaches the inflection point, the micro-scratches disappear
and the surface becomes smooth, and some grain boundary steps begin to appear vaguely. Finally, it is polished to a stable state, and the boundary step obviously covers the entire surface of the workpiece. In addition, the height of the grain boundary step obeys a normal distribution as shown in figure 10(d). The peak of the normal distribution was selected as the grain boundary step value in the model of this paper. Figure 10(e) exhibits the height of the grain boundary at different pH values. The grain boundary heights are about 2.5–3 times the surface roughness $Ra$ values.

Figure 10. Surface topographies and grain boundary steps at different polishing stages for 30 kPa. (a) Initial state, (b) inflection point, (c) steady point, (d) distribution of grain boundary height steps and (e) height of grain boundary steps under different pH value.

Figure 11 also shows that higher pressure leads to faster surface roughness reduction initially and slightly higher steady state values.

To measure the MRR, indentation marks were made on the tungsten phases before polishing. MRR was obtained by measuring the depth changes of these indentation marks after polishing. Figure 11 shows the MRR results at different pressures and pH values. As expected, the MRR increases with pressure. It is interesting to note that MRR is almost the same at pH = 4 and 7, which suggests that the MR is done mechanically. The higher MRR at pH = 10 is due to the added chemical reaction during polishing, which will be verified in section 5.4.

Figure 11. Results at different pressure and pH values.
5.4. Chemical effect analysis

Figures 9 and 11 indicate that the pH value has an impact on surface roughness and MRR. To clarify the impact mechanism, the surfaces polished by slurries with different pH values were analyzed with x-ray photoelectron spectroscopy. Our previous paper presents some preliminary experimental results [38]. The characteristic tungsten line on the surface polished in the pH = 10 slurry was significantly weakened compared with the original surface. Meanwhile, no such weakness was observed on the surface polished with the pH = 4 slurry. The weakened line of tungsten showed the reduction of tungsten atoms caused by the dissolution of tungsten in an alkaline-based condition. According to the tungsten 4f spectrum of the surface shown in figure 12, the tungsten was first oxidized to tungsten trioxide (WO$_3$), and then reacted with hydroxide (OH$^-$) dissolving into the solution. The oxidation and dissolution of tungsten grains contributed to the increase of MRR.

The height of the grain boundary step embodies of the difference between the MRR of the tungsten grains and matrix phase. In the alkaline-based slurry, the matrix phase reacted to form a soft layer, mainly composed of oxides and hydroxides, increasing the MRR of the matrix phase. The following experiments verify that oxides and hydroxides formed in the matrix phase are softer and easier to remove. The specific composition of the oxides and hydroxides requires further verification through subsequent experiments. Although the tungsten grains had a high MRR in the alkaline-based slurry, the difference between the two phases was not significantly reduced. However, some papers have proved that citric acid can inhibit the effect of grain boundaries and improve the surface of CMP [39]. Chelates produced on the surface of the matrix phase can reduce the MRR of the matrix phase, thus, reducing the difference between the MRRs of the two phases. The formation of grain boundary step is finally inhibited, as shown in figure 12(b). The specific composition of chelates and the mechanism of inhibiting MRR will be further studied in future experiments.

5.5. Model verification

The model was verified by evaluating the effects of polishing pressure, abrasive size and abrasive concentration. As shown in figure 13(a), the experimental results agree with the theoretical calculation results of the model. The boundary step was gradually enhanced with the increase of polishing pressure. This occurred because the indentation depth of tungsten alloy increases with increasing polishing pressure, and the difference of indentation depth, due to the difference of hardness, between the two phases in the tungsten alloy also increases with increasing pressure. The difference may be due to the uneven distribution of polishing slurry affected by the polishing pressure.

Figure 13(b) shows the effects of abrasive size on the grain boundary step. The applied pressure is 30 kPa and the abrasive concentration is 15 wt%. Increases in abrasive size increased the grain boundary step. The grain boundary step increases with larger particle sizes. The calculation results based on the model matched the evolution trend of the experimental results of the grain boundary step. There was a gap between the model and the experimental results, which may be due to the uneven size of the abrasive particles in experiment whereas the model assumed that the abrasives were the same size.

Figure 13(c) shows the effect of the abrasive concentration on the boundary step. The grain boundary step reduced with the increase of abrasive concentration. The calculation results based on the model matched the evolution trend of the experimental results. Under constant polishing pressure, the pressure acting on a single grinding particle decreased, and thus
the indentation depth of the abrasive particle also decreased. Moreover, the experimental results are lower than the theoretical ones under lower abrasive concentration. This may be due to the fact that more applied pressure is placed on the polishing pad than on the abrasives. In addition, the uneven distribution of abrasive particles may be another reason for the difference.

6. Conclusions

In this paper, the mechanism of boundary step generation in CMP of a W–Ni–Fe alloy was investigated, and a model of grain boundary step formation was proposed, which is also suitable for polycrystalline and multi-phase materials. The role of mechanical and chemical action was determined through experiments and analyses. The following conclusions can be drawn:

(a) The mechanism reveals that the grain boundary steps formed due to the hardness difference between the tungsten phase and the matrix phase. These grain boundary steps dominate the polished surface roughness. The steady state surface roughness is determined by the pressure, chemical reaction and abrasive particle size.

(b) Based on the formation mechanism of the grain boundary step, the proposed model can be used to predict changes in the heights of the steps based on polishing time. The theoretical model is related to the polishing pressure, abrasive size and abrasive concentration.

(c) The chemical action has a certain effect on the surface roughness and MRR. In the alkaline-based solution, the grain boundary step was suppressed, and MRR increased. The grain boundary step was further suppressed with citric acid.

(d) There is an appropriate balance between mechanical and chemical action at the inflection point. The optimum Ra < 10 nm surface roughness and high MRR were obtained in a citric acid solution at 45 kPa pressure.

This research also provides guidance for polishing other multi-phase and polycrystalline materials. Following research work should focus on optimizing polishing process parameters.

Acknowledgments

This research was supported by National Key Research and Development Program (No. 2018YFA0702900), National Natural Science Foundation of China (No. 51975096), Science Challenge Project (No. TZ2018006-0101-01) and LiaoNing Revitalization Talents Program (No. XLYC1807230).
Appendix A

MR measurement

The MRR of W–Ni–Fe alloy for lapping was calculated by the change of depth in V-shaped groove on workpiece, measured by a three-dimensional surface profiler (Talysurf PGI 840, Taylor Hobson) with vertical resolution of 0.8 nm and measuring accuracy of 0.1 µm. Since MRR during polishing is much smaller than that of lapping which is less than one-twentieth, it was decided by the MRR of tungsten particles, which was calculated by the change of indentation depth on them, measured by a laser confocal microscope (VH-X 250X, Keyence) with vertical resolution of 0.5 nm and measuring accuracy of 0.2 + L/100 µm (L is the measurement length on the depth direction). The measuring principle is shown in figure A1. These two kinds of MRR were both calculated by the following equation:

\[
\text{MMR} = \frac{h_1 - h_2}{t}.
\]  

(A1)

Where \(h_1\) is the depth of V-shaped groove or indentation before lapping and polishing, \(h_2\) is the depth of V-shaped groove or indentation after lapping and polishing, \(t\) is lapping and polishing time.

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References

[1] Kumari A, Prabhu G, Sankaranarayana M and Nandy T K 2017 Effect of solution treatment temperature and cooling rate on the mechanical properties of tungsten heavy alloy Mater. Sci. Eng. A 688 225–36
[2] Scapin M 2015 Modeling of the heavy tungsten alloy IT180 Int. J. Refract. Met. Hard Mater. 50 258–68
[3] Huang J H, Cao Z W, Zhou G A and Chen H 1999 Computer numerical simulation of mechanical properties of tungsten heavy alloys Trans. Nonferrous Met. Soc. China 9 52–56
[4] Das J, Rao G A, Pabi S K, Sankaranarayana M and Sarma B 2011 Deformation behaviour of a newer tungsten heavy alloy Mater. Sci. Eng. A 528 6235–47
[5] Şahin Y 2014 Recent progress in processing of tungsten heavy alloys J. Powder Technol. 2014 764306
[6] Arora A and Rao V G 2004 Tungsten heavy alloy for defence applications Mater. Technol. 19 210–5
[7] Tang D W, Zou S L and Yan L 2018 Research on the preparation and shielding properties of W–Ni–Fe alloy material by liquid phase sintering Powder Metall. 61 28–35
[8] Pappu S, Kennedy C, Murr L E, Magness L S and Kapoor D 1999 Microstructure analysis and comparison of tungsten alloy rod and [001] oriented columnar-grained tungsten rod ballistic penetrators Mater. Sci. Eng. A 262 115–28
[9] Miller A C, Brooks K, Smith J and Page N 2004 Effect of the militarily-relevant heavy metals, depleted uranium and heavy metal tungsten-alloy on gene expression in human liver carcinoma cells (HepG2) Mol. Cell. Biochem. 255 247–56
[10] Escobedo J P, Brown E N, Trujillo C P Cerreta E K and Gray III G T 2013 The effect of shock-wave profile on dynamic brittle failure J. Appl. Phys. 113 103506
[11] Ryu H J, Hong S H and Back W H 2000 Microstructure and mechanical properties of mechanically alloyed and solid-state sintered tungsten heavy alloys Mater. Sci. Eng. A 291 91–96
[12] Nen R, Maier H, Balden M, Dux R, Elgeti S, Gietl H and Team A U 2018 Results on the use of tungsten heavy alloys in the divertor of ASDEX Upgrade J. Nucl. Mater. 511 567–73
[13] Lorenzo P, Miralda M, Iyengar S, Melin S and Noah E 2013 Fatigue properties and characterization of tungsten heavy alloys IT180 & D176 Int. J. Refract. Met. Hard Mater. 41 250–8

[14] Nandam S R, Ravikiran U and Rao A A 2014 Machining of tungsten heavy alloy under cryogenic environment Proc. Mater. Sci. 6 296–303

[15] Suzuki N, Haritani M, Yang J, Hino R and Shamoto E 2007 Elliptical vibration cutting of tungsten alloy molds for optical glass parts CIRP Ann. 56 127–30

[16] Jiang L, Lan Y Q, He Y Y, Li Y, Li Y Z and Luo J B 2014 1,2,4-Triazone as a corrosion inhibitor in copper chemical mechanical polishing Thin Solid Films 556 395–404

[17] Shi X L, Pan G S, Zhou Y, Xu L, Zou C L and Gong H 2015 A study of chemical products formed on sapphire (0001) during chemical–mechanical polishing Surf. Coat. Technol. 270 206–20

[18] Xu W H, Lu X C, Pan G S, Lei Y Z and Luo J B 2010 Ultrasonic flexural vibration assisted chemical mechanical polishing for sapphire substrate Appl. Surf. Sci. 256 3936–40

[19] Aida H, Doi T, Takeda H, Katakura H, Kim S W, Koyama K, Yamazaki T and Uneda M 2012 Ultra-precision CMP for sapphire, GaN, and SiC for advanced optoelectronics materials Curr. Appl. Phys. 12 S41–S46

[20] Lee H S, Jeong H D and Dornfeld D A 2013 Semi-empirical material removal rate distribution model for SiO2 chemical mechanical polishing (CMP) processes Precis. Eng. 37 483–90

[21] Luo J F and Dornfeld D A 2003 Effects of abrasive size distribution in chemical mechanical planarization: modeling and verification IEEE Trans. Semicond. Manuf. 16 469–76

[22] Jeng Y R and Huang P Y 2005 A material removal rate model considering interfacial micro-contact wear behavior for chemical mechanical polishing J. Tribol. 127 190–7

[23] Qin K D, Moudgil B and Park C W 2004 A chemical mechanical polishing model incorporating both the chemical and mechanical effects Thin Solid Films 446 277–86

[24] Paul E, Kaufman F, Brusis V, Zhang J, Sun F and Vacassay R 2005 A model of copper CMP J. Electrochem. Soc. 152 G322

[25] Zhao Y W, Chang L and Kim S H 2003 A mathematical model for chemical–mechanical polishing based on formation and removal of weakly bonded molecular species Wear 254 332–9

[26] Xu Q Z, Chen L, Fang J J and Yang F 2015 A chemical mechanical planarization model for aluminum gate structures Microelectron. Eng. 131 58–67

[27] Wang Y G, Zhao Y W, Jiang J Z, Li X F and Bai J 2008 Modeling effect of chemical–mechanical synergy on material removal at molecular scale in chemical mechanical polishing Wear 265 721–8

[28] Li J, Lu X C, He Y Y and Luo J B 2011 Modeling the chemical–mechanical synergy during copper CMP J. Electrochem. Soc. 158 H197

[29] Ross D and Yamaguchi H 2018 Nanometer-scale Characteristics of polycrystalline YAG ceramic polishing CIRP Ann. 67 349–52

[30] Suzuki H, Okada M, Namba Y and Goto T 2019 Superfinishing of polycrystalline YAG ceramic by nanodiamond slurry CIRP Ann. 68 361–4

[31] Jiao Z H, Kang R K, Dong Z G and Guo J 2019 Microstructure characterization of W-Ni-Fe heavy alloys with optimized metallographic preparation method Int. J. Refract. Met. Hard Mater. 80 114–22

[32] Popov V L 2010 Contact Mechanics and Friction: Physical Principles and Applications (Berlin: Springer)

[33] Zhang J H, Kang R K, Dong Z G and Guo J 2019 Microstructure characterization of W-Ni-Fe heavy alloys with optimized metallographic preparation method Int. J. Refract. Met. Hard Mater. 80 114–22

[34] Jeng Y R and Huang P Y 2005 A material removal rate model considering interfacial micro-contact wear behavior for chemical mechanical polishing J. Tribol. 127 190–7

[35] Qin K D, Moudgil B and Park C W 2004 A chemical mechanical polishing model incorporating both the chemical and mechanical effects Thin Solid Films 446 277–86

[36] Paul E, Kaufman F, Brusis V, Zhang J, Sun F and Vacassay R 2005 A model of copper CMP J. Electrochem. Soc. 152 G322

[37] Zhao Y W, Chang L and Kim S H 2003 A mathematical model for chemical–mechanical polishing based on formation and removal of weakly bonded molecular species Wear 254 332–9

[38] Xu Q Z, Chen L, Fang J J and Yang F 2015 A chemical mechanical planarization model for aluminum gate structures Microelectron. Eng. 131 58–67

[39] Wang Y G, Zhao Y W, Jiang J Z, Li X F and Bai J 2008 Modeling effect of chemical–mechanical synergy on material removal at molecular scale in chemical mechanical polishing Wear 265 721–8

[40] Li J, Lu X C, He Y Y and Luo J B 2011 Modeling the chemical–mechanical synergy during copper CMP J. Electrochem. Soc. 158 H197

[41] Ross D and Yamaguchi H 2018 Nanometer-scale Characteristics of polycrystalline YAG ceramic polishing CIRP Ann. 67 349–52

[42] Suzuki H, Okada M, Namba Y and Goto T 2019 Superfinishing of polycrystalline YAG ceramic by nanodiamond slurry CIRP Ann. 68 361–4

[43] Jiao Z H, Kang R K, Dong Z G and Guo J 2019 Microstructure characterization of W-Ni-Fe heavy alloys with optimized metallographic preparation method Int. J. Refract. Met. Hard Mater. 80 114–22

[44] Popov V L 2010 Contact Mechanics and Friction: Physical Principles and Applications (Berlin: Springer)