PLSR-based surface damaged layer depth determination of sawed natural diamond

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Abstract
The damaged layer depth of sawed natural diamond is an important factor for evaluating the quality of the sawed surface, however, it is difficult to determine. To measure the layer depth quickly and accurately, sawed natural diamond surfaces with low roughness are obtained in this study. A roughness measuring instrument, scanning electron microscope, x-ray diffractometer, and other equipment are used to characterize and analyse the sawed surface. The results show that a cut surface with acceptable quality can be obtained by sawing natural diamond. They also show that a part of the sawed natural diamond has been transformed into amorphous carbon and carbon allotropes in the damaged layer. Based on these observations, the damaged layer depth is experimentally measured. A new method, based on x-ray diffraction and partial least squares regression, which quickly and accurately determines the damaged layer depth, is proposed. This method provides an effective means for evaluating the quality of sawed diamond surfaces.

1. Introduction

Natural diamond with its high strength and hardness, along with its good abrasion resistance thermal conductivity, and other characteristics, is not only used as gemstone jewellery but also widely used in ultra-precision machining tools, abrasive tools, various drill bits, and optical windows [1–4].

Sawing diamond will produce a damaged layer [3] on the sawed surface and result in surface stress, dislocations [6], microcrystalline strain [7], and other issues that affect the subsequent service performance of sawed the diamond [8–10]. Therefore, the damaged layer is highly significant when evaluating the service performance of the sawed diamond. As the depth of the damaged layer will directly affect the performance of the sawed diamond surface, a number of researchers have analysed the cause and influence of the damaged layer, but most of them have focused on diamond films that are easily separated and observed, rather than large granular diamonds. In addition, their works involved difficult theories and complex analytical methods and are hence not accessible for practical applications. However, these works provided the references for follow-up research. The influence of the damaged layer on diamond properties is mainly reflected in the damaged layer depth. Common detection methods for the damaged layer depth include the metallographic method, the microhardness method [11], and the acoustic display microscope method. However, the metallographic method will destroy the damaged layer structure, while the instruments for the microhardness and acoustic display microscope methods are more complex to operate. These two methods cannot accurately and quickly detect the depth of the damaged layer under time or experimental conditions constraints.

A new method combining x-ray diffraction and partial least squares regression (PLSR) [12] is proposed to determine the depth of the damaged layer. Based on the principle of x-ray diffraction, the diffraction pattern and related data of the sawed diamond surface are obtained and the unknown damaged layer depth is determined by PLSR, realizing the rapid and accurate determination of the damaged layer depth. The depth can guide the performance evaluation and subsequent production processing of the sawed diamond.
2. Sample selection and surface quality characterization

2.1. Sample selection
There are multiple ways that can be used to cut natural diamond, such as laser processing [13] and sawing. Laser processing creates cracks and faults on the cut surface of the diamond and produces graphite. Hence, laser processed diamond is unsuitable for analysis through our methods. Sawing produces better quality cut surfaces with fewer cracks and faults. Therefore, we obtained our samples by sawing. The samples are natural octahedral diamonds imported from Australia with a purity of about 99.99% and a weight between 1.1 and 1.6 ct. A traditional diamond cutting machine was used, as shown in Figure 1.

As shown in Figure 1, the saw blade used in the diamond cutting machine is a phosphorous bronze saw blade. The diameter, thickness, and speed of the saw blade are 80 mm, 0.06 mm, and 3000 r/min, respectively and the edge of the saw blade was coated with abrasive paste mixed with diamond powder and olive oil. The diamond was cut along the (110) crystal surface. After cutting, the obtained cut surface of the natural diamond was placed under an optical microscope with 500 times magnification. The observed surface morphology of the cut surface is shown in Figure 2.

As shown in Figure 2, different degrees of scratches and tool marks on the machined surface were obtained after cutting. However, these scratches and tool marks reflect only the surface morphology of the damaged layer on the cut surface from a macro perspective. They cannot explain the material and performance changes from a micro perspective, nor can they be used as the standard for evaluating the surface quality of the cut surface.

Therefore, to further understand the damaged layer and develop a method to evaluate the performance of the cut surface, roughness measurement, scanning electron microscopy, and x-ray diffraction (XRD) were employed for further characterization and analysis of the cut surface.

2.2. Characterization and analysis of cut surface quality
In the field of precision and ultra-precision machining, the surface roughness is an important evaluation criterion for evaluating the processing quality of the workpiece. The surface roughness measured by appropriate instruments reflect the distribution characteristics of the peaks and troughs of the workpiece surface micromorphology. A VEECO NT1100 surface roughness measuring instrument was used to characterize the cut surface of natural diamond is an area where the surface was smooth and parallel to the (110) crystal surface. The characterization results are shown in Figure 3.

As shown in Figure 3, the detected roughness is 91.10 nm, and the direction of the groove is along the [1-10] crystal direction. Repeated testing gave very close values of the roughness. Therefore, the roughness does not reflect the surface quality of the cut surface damaged layer well. To obtain a more comprehensive understanding of the damaged layer, a scanning electron microscope was used to observe the cut surface from a micro perspective.

A ZEISS EVO MA25 scanning electron microscope from Germany was used to observe the micro-structure of the smooth area on the cut surface. Since natural diamond does not conduct electricity, the diamond was plated with gold for observation by the scanning electron microscope. The cut surface to be measured was
cleaned with alcohol to remove any contaminations and then gold-plated. After gold-plating, the (110) crystal plane of the cut crystal was observed under the scanning electron microscope, as shown in figure 4.

From figures 4(a) and (b), it can be observed that the surface of the natural diamond is mostly smooth and flat. As shown in figure 4(a), grooves left by crystal stripping are present. There is a structure shown in figure 4(b) which looks like a mountain on the cut surface. By analysing the morphology of the structure, it was concluded that the structure is caused by the defects of diamond already present before sawing. Generally speaking, sawing creates many different micro-defects on the cut surface, which is inconsistent with the roughness detection results. Moreover, the roughness and micro-structure can only reflect the surface conditions of the damaged layer on the cut surface but cannot explain the internal composition and properties of the damaged layer. The x-ray diffractometer can detect and analyse the internal material composition and changes in the damaged layer on the cut surface, which is of great help in further research on the damaged layer. Therefore, the damaged layer of the cut surface was further analysed by a x-ray diffractometer.

The sample was irradiated by x-ray from the x-ray diffractometer, and the unique diffraction pattern of the sample obtained [14]. The diffraction pattern was matched with the standard PDF cards in the database of the professional analysis software Highscore (Plus). The matched PDF card contains various microscopic parameters of the matched material. The x-ray diffractometer used in this experiment is the EMPYREAN Ruki Series 2 produced by the Dutch company PANalytical. The x-ray produced by this equipment was obtained by using copper-alpha radiation. The phase detection analysis of the natural diamond (110) crystal plane was carried out by the x-ray diffractometer, and the following results were obtained.

As shown in figure 5, the sample has the diffraction pattern of the (110) crystal plane of the natural diamond. The upper left corner of the diffraction pattern indicates the types of allotropes contained in the tested sample. The percentage content of each allotrope was obtained by refining the pattern with Highscore (Plus). Through comparison with the software database, it was found that these allotropes are diamond and diamond-like allotropes, such as lonsdaleite (hexagonal diamond) and other variants with different stacking of (111) layers.
Therefore, during the process of sawing, the crystal structure of diamond was slightly changed by the change of force and the removal of material. Although there are some differences in the structure of these diamonds, they are still diamonds in essence. There may be some distortions resulting from the cutting process, but these distortions will not affect the final results. In the database of Highscore (Plus), there are various PDF cards of

**Figure 4.** Surface structure of diamond cut surface under the scanning electron microscope. (a) Groove. (b) A mountain like structure.

**Figure 5.** XRD phase detection analysis of cut surface with the (110) crystal orientation.
different substances. The substance on each PDF card has a specific peak position. The peak positions on each card is compared with the peaks of the measured sample. If the angles are the same, then the match is completed, proving that the substance on the PDF card is the same as that in the sample. The upper left corner of figure 5 indicates the number of the PDF card and the percentage content of the corresponding allotrope. In this diffraction pattern, there is a very obvious peak, which is the diamond (110) peak. In addition, there are several other peaks that are much less intense than the diamond (110) peak. These peaks are only slightly higher than the background and cannot be clearly seen in the diffraction pattern in figure 5. The vertical lines in figure 5 are the results of matching the peak positions of the allotropes on the cards with those of the diffraction pattern. The x-ray diffractometer phase detection on the diamond cut surface, found that in addition to diamond, amorphous carbon and various allotropes of carbon are present on the cut surface, but graphite is absent. The results show that sawing will not lead to the graphitization of natural diamond, but it will lead to the transformation of diamond to amorphous carbon and carbon allotropes. Hence, the impurities in the damaged layer of the cut surface are mainly composed of amorphous carbon and carbon allotropes. The influence of the damaged layer on the service performance of diamond is mainly reflected in the damaged layer depth. If the depth can be determined quickly and accurately, the service performance of the diamond cut surface can be better evaluated.

PLSR [12] is a multivariable statistical analysis method used for discriminant analysis. It seeks the best match between the data and matching functions by minimizing the square of the error, and predicts particular results by performing regression modelling of multi-dependent variables and independent variables. A PLSR method based on x-ray diffraction is proposed in this study. A determination model of the damaged layer depth based on x-ray diffraction and PLSR was built in Highscore (Plus) to quickly and accurately determine the damaged layer depth. The depth determined by the model was compared with the actual depth of the damaged layer depth measured by experiments to verify the accuracy of the model.

3. Determination of damaged layer depth and experimental comparisons

The samples for the determination of the damaged layer depth consisted of three (110) cut surfaces with low roughness and similar surface quality to exclude the influence of irrelevant factors on the results. The three samples were sequentially numbered as samples 1, 2, and 3. The diamond surface information detected by the x-ray diffractometer was first used as the reference data. The PLSR-based depth determination model was then built by Highscore (Plus). The establishment of the model was completed by software and did not require manual modelling. The model was then used to determine the damaged layer depth of the machined diamond surface.

3.1. Determination of the damaged layer depth by PLSR

X-ray diffraction patterns of diamond cut surfaces with known damaged layer depths were obtained by the x-ray diffractometer. The material parameters of each pattern, including the cell parameters, crystal plane spacing, and microcrystalline strain were different. These diffraction patterns were input into Highscore (Plus) and fitted in the same interface during the modelling process after which the model was saved. The diffraction pattern of the diamond cut surface for which the damage layer depth was to be determined was then imported into Highscore (Plus), which compared the pattern with the established model. The comparison was completed by the software and no manual input was required. After the comparison, Highscore (Plus) automatically calculated the damaged layer depth. The process of model matching and calculation were all completed through options in Highscore (Plus) without the need for human programming or other manual input.

Owing to the anisotropies and properties of the diamond materials, the intensities and shapes of the diffraction peaks were different when the same position of the sample was measured by x-rays from different angles. Therefore, in order to improve the accuracy, three x-ray measurements were taken at the three measurement positions used for comparative analysis. Taking the (110) crystal plane as an example, rotating the diamond cut surface horizontally changed the x-ray incident angle at a given position. Three diffraction patterns at the rotation angles of 0°, 45°, and 90° were obtained and merged. The diffraction patterns were imported via the interface of Highscore (Plus) to obtain the crystal characteristics at different angles.

As shown in figures 6–8, the diffraction patterns at the three measured positions show similar roughness. The positions, shapes, and strengths of the peaks in the three diffraction patterns are different from one another. Therefore, when using Highscore (Plus) to construct the PLSR determination model, it is necessary to use three different incident angles at each position to ensure the accuracy of the model determination results. In order to obtain the optimal values of the model factors, one to six positions, each with three recordings of data, were modelled to obtain the determination model. After comparing the damaged layer depth obtained by the determination model with the experimental data, it was found that the determined value was closest to the
Figure 6. Diffraction patterns of sample 1 at different x-ray incident angles.

Figure 7. Diffraction patterns of sample 2 at different x-ray incident angles.

Figure 8. Diffraction patterns of sample 3 at different x-ray incident angles.
experimental date when five positions, each with three recordings of data, were selected for modelling. Thus, five positions each with three recordings of data, as shown in figure 9, were selected for modelling to obtain the model which can effectively predict the damaged layer depth.

In the determination model shown in figure 9, five positions were selected, and 15 diffraction patterns were recorded, each of which contained different data. Through the cluster analysis [15] of the 15-group data by Highscore (Plus), different factors were obtained, each of which influenced the modelling determination results differently. These factors thus need to be screened. The model determinations for the obtained factors were performed and the results were evaluated. The evaluation results showed that the optimal effect was achieved when modelling with six correlation factors, so six correlation factors were selected for further modelling. Finally, Highscore (Plus) was used to construct a determination model for the damaged layer depth of the natural diamond cut surface, and the damaged layer depth was determined using the model. In this way, the damaged layer depth can be directly determined from the diffraction pattern, thereby achieving great time saving in the performance evaluation.
3.2. Comparison of determined depths with actual values
Before grinding, the diamond cut surface was cleaned, soaked, and wiped with alcohol to ensure that no residues were left from the cutting process. Then, XRD was used to obtain the diffraction pattern of the sample, determine the amorphous carbon and carbon allotropes content at the detected position, and mark the detected position. The position containing the amorphous carbon and carbon allotropes was ground. The specific ground area ranged from the initial ground position to the position just covered by the XRD measurement. The ground area of the sample was polished by sandpaper covered with silicon carbide abrasives immersed in alcohol, and wiped with alcohol every minute. The position of the diffraction pattern recorded prior to the grounding was analysed by phase analysis and then ground again repeatedly until the amorphous carbon and carbon allotropes on the cut surface disappeared. After several rounds of grinding and XRD detection, the (110) crystallographic cut surface without amorphous carbon and carbon allotropes was finally obtained. The phase detection result of one of the crystal surfaces meeting this standard is shown in figure 10. The three samples that met the standards have been ground 32, 38 and 43 times.

The VEECO NT1100 roughness measuring instrument was used to measure the ground boundary area many times, and the grinding depth was characterized using the three-dimensional characterization function of the equipment. To reduce the experimental error, each sample was measured 10 times, the maximum and minimum values were removed, and a group value close to the average value was taken as the final result.

Figure 11. Measurement results of sample 1. (a) Vertical view of roughness at the grinding boundary. (b) Front view of the height change.
detection results are shown in figures 11–13. As shown in part (a) of each figure, the smooth part on the left is the part that has been ground while the part on the right has not been ground. In part (b), the thickness of the damaged layer was obtained from the height difference between the ground and unground parts. Specifically, the heights were taken at positions 0.2 mm to the left and right of the boundary between the ground and unground segments. The depth of the damaged layer is calculated as the height difference between these two positions. The left side of the figure is lower because of grinding.

As shown in figure 11, the mean of the measured value of sample 1 is about 0.301 μm, indicating that its damaged layer depth is 0.301 μm.

As shown in figure 12, the mean of the measured value of sample 2 is about 0.353 μm, indicating that the damaged layer depth is 0.353 μm.

As shown in figure 13, the mean of the measured value of sample 3 is about 0.426 μm which shows that the damaged layer depth is 0.426 μm.

Under normal conditions, the material removal rate should decrease with repeated grinding processes. Therefore, the maximum error can be estimated by replacing the error produced by the last grinding with the average depth of each grinding. By dividing the final grinding depth by the number of grinding repetitions, the
average depth of each grinding repetition can be obtained. The error of each measurement result is estimated using the final detection result and grinding times as shown in table 1.

As shown in the table, the maximum error value is no more than 10 nm, indicating that the measurement of the damaged layer depth is highly reliable.

The results of 15 measurements of the damaged layer depth were obtained through the above methods, and PLSR was used to determine the damaged layer depth in these measurements. The experimental values and the values determined by PLSR were compared. The results are shown in table 2.

The comparison between the experimental values and values determined by PLSR demonstrate that the determined results are very reliable. Therefore, PLSR can be used to determine the damaged layer depth of cut surfaces on natural diamond quickly and accurately.

Table 1. Errors in each detection result.

| Sample number | Sample 1 | Sample 2 | Sample 3 |
|---------------|----------|----------|----------|
| Error (nm)    | <9.5     | <9.3     | <9.9     |
4. Conclusion

Through the characterization and analysis of cut surfaces on natural diamond obtained by sawing, it was found that the processed diamond surfaces contain different forms of damage, and that their performance cannot be effectively evaluated from surface roughness alone. The impurities in the processed diamond surface are mainly composed of amorphous carbon and carbon allotropes. A new method based on x-ray diffraction and PLSR for measuring the damaged layer depth of diamond cut surfaces obtained by sawing was proposed. The experimental results show that the errors between the determined and true values are small. Therefore, this study provides a new, accurate, and efficient scientific method for evaluating the surface quality of cut surfaces on natural diamond.

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