The influence of sintering parameters on the mechanical properties of vitrified bond diamond tools

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A B S T R A C T

The aims of this study were to investigate the influence of sintering parameters on the mechanical properties of vitrified bond diamond tools. All of the sintered specimens were examined using a thermal analyzer, an X-ray diffraction analyzer, an X-ray photoelectron spectrometer analyzer, a Raman spectrometer analyzer and a scanning electron microscope. The mechanical properties of the sintered specimens including the radial shrinkage percentage, sintered density, hardness and grinding ratio were also recorded. Experimental results showed that the introduction of nitrogen at a sintering temperature of 500 °C could prevent diamond grit from reacting with oxygen and prevent diamond crystals from forming a graphite structure. The microstructure of the sintered specimen 710-90 indicated that the vitrified matrix and diamond grit had excellent coverage and wetting. After the grinding ratio tests, the surface of the vitrified matrix of specimen 710-90 revealed a brittle failure pattern, indicating that the diamond grit could be easily pulled from the vitrified matrix when the diamond grit was worn and the cutting force increased. Therefore, the diamond grit always kept its sharpness and the workpiece maintained the preferred surface roughness. In this study, specimen 710-90 had the best mechanical properties and highest grinding ratio (57.5).

1. Introduction

The unique physical and mechanical properties of diamonds make them the preferred choice in a range of applications, including those in electronics, precision optics, precision machinery, automobiles, biomedical, national defense, earthworks and aerospace [1–6]. Diamond tools are a group of composite materials composed of diamond grit and a bonding matrix. Familiar bonding materials include metals, resins, vitrified glass, and electroplating. As vitrified bond diamond tools can be densified by pressureless sintering at low temperatures, pores of different sizes can be introduced into the tool structure [3,4,7,8]. Such a structure can possibly reduce the frictional heat generated during working by reducing the contact area and by allowing for the flow of cooling fluid into the pores [8–10].

The vitrified matrix should provide a suitable brittleness, thus when the diamond grit is worn and the cutting stress increases, the bond can break and release the worn diamond grit from the matrix. In other words, vitrified bond diamond tools should possess an excellent capacity for self-dressing. To improve the bonding force between the diamond grit and vitrified matrix, a suitable matrix toughness and hardness are required. A good wetting ability, gradual chemical reactions, and similar thermal expansion coefficients between the diamond grit and the matrix are also required [9,10]. Uniform pore distribution within the vitrified matrix is very important for chip removal and reduction of frictional heat generated during the cutting process. Additionally, reduction of the sintering temperature and introduction of a protective atmosphere are considerably important during the sintering process in order to prevent the graphitization of diamonds due to high temperatures, which would result in decreased performance of the diamond tools [11–14].

In this study, a borosilicate glass and diamond grit were selected to make vitrified bond diamond tools, and various sintering parameters were used. All of the sintered specimens were examined by thermal analysis, X-ray diffraction (XRD) analysis, X-ray photoelectron spectroscopy (XPS) analysis, Raman spectroscopy analysis, and various mechanical performance tests. The aims of this study were to clarify the influence of sintering parameters on the mechanical properties of vitrified bond diamond tools and to provide optimal sintering parameters for vitrified bond diamond tools.

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2. Experimental procedure

The composition of the specimens used in this study had a 1:3:1 volume ratio of diamond grit, glass, and paraffin wax. The paraffin wax was used to lubricate each specimen during the die-pressing process. The mean particle size of the diamond grit was 30.7 μm (GE, FM 30–40) and the glass powder was 16.7 μm (China Glaze, CT-1124). Table 1 shows the composition of the glass powder. The diamond grit and glass powder mixture were first mixed with 20 vol% paraffin wax, which was dissolved in heptane, and then blended in a plastic jar using tetragonal zirconia polycrystal balls. The milled powder slurry was heated at 60 °C for 90 min to remove the heptane, and granules were formed by sieving the dried mixture by using a 100-mesh sieve. After the granule-forming process, the powders were then die-pressed into the specimens. Round-shaped specimens, having 3 mm thickness and outer diameters of 12 mm and 30 mm, respectively, were die-pressed with a pressure of 30 MPa. The specimens were then placed on a high-density graphite plate and sintered in a tube furnace with various temperatures and isothermal holding times. Table 2 shows nine sintering parameters for the specimens.

The thermal profile was composed of heating at 5 °C/min to 250 °C, a temperature which was then maintained for 30 min to burn off the paraffin wax, followed by a continuing rise in temperature of 3 °C/min to 620 °C, a temperature which was then held for 60 min. This schedule was followed directly by heating at 1 °C/min to 690 °C, 710 °C, or 730 °C, with each of these temperatures held for 60, 90, or 120 min. All the specimens were furnace-cooled. An air atmosphere was maintained until isothermal holding at 500 °C. Then, at that temperature, the atmosphere was changed to nitrogen to protect the diamond grit from oxidation.

The thermogravimetric analyzer (TGA, TA Instrument Thermal Analysis Q500) carried out thermal analysis for the glass powder and diamond grit. A heating rate of 5 °C/min, from room temperature (R.T.) to 1000 °C was executed. A differential scanning calorimetry test (DSC, HT-DSC, Netzsch Instrument 404) was carried out for the glass powder in order to find out its glass transition temperature. A heating rate of 5 °C/min from R.T. to 900 °C was executed. Sintered specimens were also examined by XRD analysis. The X-ray diffractometer (Shimadzu, XRD-6000) used 30 kV voltage [15–18]. Table 1 shows the composition of the glass powder. The composition of the glass powder used in this study was approximately 716 °C.

2.3. Raman spectroscopy analysis

The specimens sintered at different temperatures for the same isothermal holding time of 90 min (690-90, 710-90, and 730-90), and those with the same sintering temperature of 710 °C but different isothermal holding times (710-60, 710-90, and 710-120) were examined by XRD. All XRD patterns showed three diffraction peaks, the 2θ angles were 44.3°, 75.5°, and 91.7°, respectively, which approach the diffractions angles of (1 1 1), (2 2 0), and (3 1 1) planes of diamond [18,19]. Therefore, within the experiment range of this study, no phase other than diamond was observed after changing the sintering temperature and isothermal holding time.

3. Results and discussion

3.1. Thermal analysis

TGA analysis of the diamond grit showed no weight loss from 25 °C to 600 °C; however, a rapid weight loss was observed between 630 °C and 725 °C due to the fact that diamonds react with oxygen [15–18]. TGA analysis of the glass and paraffin wax showed a weight loss between 180 °C and 350 °C. A differential of TGA data exhibited that the volatilization temperature of paraffin wax was around 204 °C. DSC analysis showed that the glass transition temperature (Tg) for the borosilicate glass powder used in this study was approximately 716 °C.

3.2. XRD analysis

Fig. 1(a) shows the Raman spectra for specimens 690-90, 710-90, and 730-90, respectively. A sharp peak at 1333.4 cm⁻¹ can be observed which belongs to the crystalline diamond C—C bond D-band signal. This indicated that the analyzed object was a diamond with the SP³ structure [20,21]. The amorphous carbon generated on the diamond surface and the changed diamond crystal was possibly due to the increase in sintering temperature or isothermal holding times. Fig. 1(b) shows that the Raman spectra of the specimens with different isothermal holding times (710-60, 710-90, and 710-120) were similar; no G-band signals belonging to the SP² graphite structure were detected. It is particularly noteworthy that the intensity of D-band signal decreased with the increase in sintering temperature or isothermal holding.
which indicates that the degradation of diamond grit becomes more serious with high sintering temperatures or prolonged isothermal holding [21,22]. In this study, the influence of the sintering temperature was greater than that of the isothermal holding.

3.4. XPS analysis

XPS analysis was carried out for the specimens to further investigate the bonding structures between the diamond grit and the vitrified matrix. Fig. 2 shows the XPS spectrum profiles of C1s for the sintered specimen 710-90. Table 3 lists the XPS analysis C1s bond ratio of the specimens 690-90, 710-90, and 730-90, respectively. It was found that when the sintering temperature increased from 690 °C to 710 °C, the proportions of C–C (69.7%) and C–B (30.3%) bonds increased; however, when the sintering temperature increased to 730 °C, the proportions of C–C (52.3%) and C–B (16.4%) bonds decreased. As the bonding energy of C–C bonds is higher than that of C–B bonds, when the sintering temperature increased from 690 °C to 710 °C, the bonding forces within the diamonds increased. However, when the sintering temperature increased to 730 °C, the proportion of C–C bonds decreased, thus lowering the bonding forces within the diamonds.

With regards to C–B bonds, after increasing the sintering temperature to 710 °C, the proportion of C–B bonds increased, thus the bonding forces between the diamonds and the vitrified matrix was strengthened. However, when the sintering temperature increased to 730 °C, the high sintering temperature resulted in lower bonding forces. Table 3 also lists the XPS analysis N1s bond ratio for specimens 690-90, 710-90, and 730-90. The proportions of N–C and N≡C bonds increased as the sintering temperature increased, indicating that increases in sintering temperature increase the bonding of nitrogen and carbon. On the other hand, after increasing the sintering temperature, the proportion of N–B bonds decreased, indicating the reactions between the nitrogen and the vitrified matrix decreased.

Table 4 shows the XPS analysis C1s bond ratio for specimens 710-60, 710-90, and 710-120, respectively. When the isothermal hold increased from 60 min to 90 min, the proportion of C–C (69.7%) bonds increased. However, when the isothermal holding time was increased to 120 min, the proportion of C–C (54.0%) bonds gradually decreased. The proportion of C–B bonds gradually decreased as well when the isothermal holding time was increased from 60 min to 120 min. According to the above results, at a sintering temperature of 710 °C, the bonding force between the diamond and the vitrified matrix gradually decreased when the isothermal holding time exceeded 60 min. Comparison of the above three specimens found that specimen 710-90 had an optimal bonding combination.

Fig. 3 shows XPS spectrum profiles for N1s in the sintered specimen 710-90. Table 4 also shows the XPS analysis of N1s

![Fig. 1. Raman spectra of the specimens: (a) 690-90, 710-90, and 730-90; (b) 710-60, 710-90, and 710-120.](image)

![Fig. 2. XPS spectrum profiles for sintered specimen 710-90 (C1s).](image)

![Fig. 3. XPS spectrum profiles for sintered specimen 710-90 (N1s).](image)
bond ratios for specimens 710-60, 710-90, and 710-120, respectively. As the isothermal holding time was increased, the proportion of N–C and N=≡C bond gradually decreased, but the proportion of N–B bonds increased. It can be concluded that at a sintering temperature of 710 °C, increasing the isothermal holding time decreases the proportion of N–C bonds generated at the diamond surface, and increases the proportion of N–B bonds between the nitrogen and vitrified matrix.

3.5. Microstructure analysis

Fig. 4(a) shows the SEI for the sintered specimen 690-60. The sintering temperature of the specimen was lower than the glass transition temperature \( T_g = 716 °C \) and the isothermal holding time was only 60 min. While some of the glass particles began to coalesce, overall, they mostly remained in their original particle state, resulting in inadequate bonding between the diamond grit and the glass matrix. When the isothermal holding time was increased to 90 min, necking among glass particles was obvious, but pores of various sizes were still observed in the microstructure (Fig. 4(b)). The bond between the diamond grit and the glass matrix was still weak as the glass did not have a large area of intimate coverage over the diamond grit. With an isothermal holding time of 120 min, the number of pores was obviously reduced and most of the diamond grit had intimate coverage by the glass matrix. The wetting between the diamond grit and vitrified matrix was excellent (Fig. 4(c)).

Fig. 5(a) shows the SEI for specimen 710-60. The sintering temperature was very close to the glass transition temperature; therefore, the fluidity of the glass phase increased. However, as the isothermal holding time was only 60 min, the glass matrix still had large pores of over 25 \( \mu \text{m} \); thus, a proper structure for the diamond tool was not achieved. When the isothermal holding time was increased to 90 min, the bonding and wetting of the diamond grit and the glass matrix increased and the pores in the glass matrix decreased in size to a range of 10–20 \( \mu \text{m} \) (Fig. 5(b)). These sizes of pores among the diamond grit and vitrified matrix could store the cutting fluid and be used for heat dissipation in the grinding process. When the isothermal holding time was increased to 120 min, the number of pores in the vitrified matrix was reduced noticeably. Some regions were fully densified and most of the diamond grit was completely covered by the vitrified matrix (Fig. 5(c)).

The SEI for specimen 730-60 shows an over-vitrified matrix with only a few observable pores (Fig. 6(a)). When the isothermal holding time was increased to 90 min, the vitrified matrix and diamond grit were fully densified and there were almost no pores (Fig. 6(b)). At an isothermal holding time of 120 min, the over-vitrification was more severe and cracks on the surface of the vitrified matrix were observed (Fig. 6(c)).

3.6. Radial shrinkage percentage and sintered density

The radial shrinkage percentages for sintered specimens 690-60, 690-90, and 690-120 were 9.5%, 10.5%, and 11.9%, respectively. The sintered densities for the three specimens were 2.23 g/cm\(^3\), 2.31 g/cm\(^3\), and 2.38 g/cm\(^3\), respectively. It could be observed that at a sintering temperature of 690 °C, the radial shrinkage percentage and sintered density increased as the isothermal hold increased (Fig. 7(a)). The radial shrinkage percentages for sintered specimens 710-60, 710-90, and 710-120 were 10.6%, 12.8%, and 13.7%, respectively. The sintered densities for the three specimens were 2.41 g/cm\(^3\), 2.47 g/cm\(^3\), and 2.52 g/cm\(^3\), respectively. The radial shrinkage percentage and sintered density increased as the isothermal hold increased (Fig. 7(b)).

The radial shrinkage percentages for sintered specimens 730-60, 730-90, and 730-120 were 13.0%, 12.6%, and 12.0%, respectively. Increasing the isothermal holding time from 60 min to 120 min reduced the radial shrinkage percentage by 8.3%. The sintered densities for the three specimens were 2.39 g/cm\(^3\),

![Fig. 4. SEM microstructure images for sintered specimens (a) 690-60, (b) 690-90, and (c) 690-120. (D: diamond grit, M: vitrified matrix).](image-url)
2.37 g/cm³, and 2.35 g/cm³, respectively. Increasing the isothermal holding time from 60 min to 120 min reduced the density by 1.7%. This observation indicates that at a sintering temperature 730 °C, the radial shrinkage percentage and density gradually decreased as the isothermal holding time increased (Fig. 7(c)). Because the sintering temperature of 730 °C was higher than the glass transition temperature (716 °C), and because the isothermal holding duration was prolonged, a glass phase with a lower viscosity was
formed. The glass phase flowed toward the outside due to the effect of gravity, and accordingly the radial shrinkage percentage and sintered density were decreased.

### 3.7. Hardness

The average micro Vicker's hardness for sintered specimens 690-60, 690-90, and 690-120 were 521.3, 529.2, and 538.9, respectively. The hardness of the vitrified matrix increased with an increase in isothermal holding time (Fig. 8). Such an observation is believed to arise from the decrease in pore percentage, thus increasing the vitrified matrix hardness. The average micro Vicker's hardness for sintered specimens 710-60, 710-90, and 710-120 were 546.2, 574.1, and 599.3, respectively. The sintering temperature 710°C was very close to the glass transition temperature, thus the fluidity of glass phase increased. The glass phase promptly filled in the pores as the isothermal holding time was increased. For this reason, the matrix hardness for specimens sintered at 710°C increased obviously compared to the specimens sintered at 690°C. The average micro Vicker's hardness for sintered specimens 730-60, 730-90, and 730-120 were 602.7, 609.2, and 610.8, respectively. It can be observed that increasing the isothermal holding time from 60 min to 120 min only increased the vitrified matrix hardness by approximately 1.3%. This result was possibly due to the fact that the sintering temperature 730°C surpassed the glass transition temperature. The pores in the matrix were already filled by glass during sintering. Therefore, increasing the isothermal holding time had less effect on the matrix hardness when compared with increasing the sintering temperature.

### 3.8. Grinding ratio

The grinding ratios for specimens 690-60, 690-90, and 690-120 were 4.8, 9.1, and 10.5, respectively (Fig. 9). The grinding ratios gradually increased as the isothermal holding time was increased. It was found that the grinding ratio and vitrified matrix hardness had a positive correlation. The grinding ratios for specimens 710-60, 710-90, and 710-120 were 20.2, 57.5, and 38.6, respectively. Increasing the isothermal holding time from 60 min to 90 min raised the grinding ratio by 184.7%. According to the SEI of specimen 710-90 shown in Fig. 5(b), there was excellent coverage and wetting between the diamond grit and vitrified matrix. The matrix contained a suitable amount of pores allowing the diamond grit to fall off after abrasion. Accordingly, specimen 710-90 had the highest grinding ratio. The hardness of the vitrified matrix is not the only factor that determines the grinding ratio of the diamond tool. The microstructure also affects the grinding ratio of the diamond tool.

The grinding ratios for specimens 730-60, 730-90, and 730-120 were 29.7, 36.0, and 32.4, respectively. The microstructures and hardness of these specimens were very similar; however, the
grinding ratio for 730-120 was lower than that for 730-90, probably due to the tiny cracks on the surface of the vitrified matrix in specimen 730-120. Moreover, compared to specimen 710-90, the matrix in specimen 730-90 was too dense and over-vitrified. An over-vitrified matrix without a porous structure has poor heat dissipation and thermal stress is prone to trigger cracking in the vitrified bond. In addition, diamond grit in a non-porous structure cannot be easily pulled out, which may decrease the grinding ratio.

3.9. Microstructure analysis after grinding tests

Fig. 10(a) shows the SEM microstructure image for sintered specimen 690-60 after grinding tests. The diamond grit exhibited good cutting ability during the grinding test, but as the vitrified matrix had a large number of pores, it was thus unable to efficiently retain the diamond grit. Some of the diamond grit may have been pulled out before being completely worn; accordingly, the grinding ratio of this specimen (4.8) was relatively poor. It can be observed that the number and size of pores in specimens 690-90 and 690-120 were smaller than that in 690-60 after grinding tests; therefore, they had higher grinding ratios than specimen 690-60.

Fig. 11(a) shows the SEM microstructure image for sintered specimen 710-60 after the grinding tests. Although the vitrified matrix still contained some large pores, the bond between the matrix and diamond grit was noticeably better than that for specimen 690-60. Fig. 11(b) shows the SEM microstructure image for sintered specimen 710-90 after the grinding tests. The bond between the vitrified matrix and diamonds was strong, but the surface of the matrix showed patterns of brittle failure. Such a phenomenon allowed the diamond grit to be easily pulled from the vitrified matrix after being worn. For this reason, this specimen had the highest grinding ratio (57.5). The microstructure for specimens 710-120 and 710-90 were similar. Nevertheless, the strengthened bond between the matrix and diamonds resulted in worn diamond grit being unable to be easily pulled from the matrix, thus decreasing the grinding ratio to 38.6.

The SEM microstructure image for sintered specimen 730-60 after the grinding tests shows a smooth surface due to an over-vitrified matrix (Fig. 12(a)). A nearly fully densified structure prevented the diamond grit from being pulled out from the vitrified matrix after being worn, thus reducing the grinding ratio (29.7) of the diamond tool. In addition, the low grinding ratio for specimen 730-60 may be attributed to the few pores of several micrometers in size that existed within the bonding matrix. The microstructure images for specimens 730-90 and 730-120 were similar to that of specimen 730-60. The only differences were an increase in the number and size of circular pores within the vitrified matrix (Fig. 12(c)). It was inferred that circular pores were created by the nitrogen during sintering.
A high grinding ratio and good workpiece surface roughness are required for optimal diamond tools. In this study, specimen 710-90 had the highest grinding ratio (57.5) and good workpiece surface roughness (Ra = 0.35). The matrix in specimen 710-90 had a moderate hardness, and thus offered a proper bond strength between the diamond grit and vitrified matrix. The brittle fracture structure of the vitrified matrix allowed the diamond grit to be pulled out when the diamond grit was worn and the cutting force.
was increased. The diamond grit always kept its sharpness and the workpiece maintained the preferred surface roughness (Fig. 13(b)).

The diamond grit in specimen 690-60 lacked the proper bond force and was quickly pulled from the matrix; thus it had a lower grinding ratio (4.8). The workpiece’s surface roughness was only (Ra = 0.58), inferior to that of specimen 710-90. On the other hand, specimen 730-120 had an over-vitrified matrix and the diamond grit was very difficult to pull from the matrix; this reduced its self-dressing ability. The surface roughness (Ra = 0.56) of the workpiece was also worse than that of specimen 710-90.

4. Conclusions

Raman analysis only detected the C–C bond D-band peak which belongs to a diamond crystalline structure. This observation indicates that the introduction of nitrogen can prevent diamond crystals from transforming into a graphite structure when diamond tools are sintered at over 500 °C. XPS analysis showed that maintaining a specimen isothermal holding time of 90 min and increasing the sintering temperature from 690 °C to 710 °C increased the proportions of C=C and C–B bonds and strengthened the bonds between diamonds and in the diamond-matrix. However, when the sintering temperature was increased to 730 °C, the proportions of C=C and C–B bonds decreased. The hardness of the vitrified matrix increased with an increase in isothermal hold duration and sintering temperature. However, the hardness of the vitrified matrix is not the only factor that determines the grinding ratio of the diamond tool. The microstructure also affects the grinding ratio of the diamond tool. Grinding test results showed that the specimens sintered at 690 °C provided low grinding ratios due to weak bonding which could not efficiently hold on to the diamond grit. The specimens sintered at 730 °C had an over-vitrified matrix which prevented the diamond grit from being pulled from the matrix and decreased the self-dressing ability of the diamond tools. High sintering temperatures also caused the graphitization of diamond grit and decreased the grinding ratio. Increasing the isothermal holding time achieved a high bonding strength but caused the graphitization of diamond grit; however, insufficient isothermal holding time resulted in inadequate bonding strength. The specimen sintered at 710 °C with an isothermal holding time of 90 min had the highest grinding ratio and the best workpiece surface roughness. In this study, the influence of sintering temperature on the mechanical properties of diamond tools was clearly greater than that of the isothermal holding time.

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