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Influence of Diamond Seed Attachment Processing on Diamond Films Synthesized on Tungsten Carbide Substrate by Flame Combustion

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Abstract: The flame combustion method enables the synthesis of diamonds via acetylene-oxygen gas flame combustion in ambient air. Tungsten carbide (WC) has recently been utilized as a cutting tool in the machining industry and in dental machining applications. To obtain high-quality diamond films and achieve good adhesion on a WC substrate, diamond films are synthesized on a WC substrate by the flame combustion method. However, the surface roughness of most of the diamond films synthesized by this method increased, and it was necessary to reduce this roughness. Considering the roughness accuracy of the workpiece surface during cutting, and the performance of the cutting tool, a smaller surface roughness of the diamond films synthesized is desirable. In this study, to reduce surface roughness, the amount of diamond paste with diamond seed particles as generation nuclei was carefully varied for diamond seed attachment processing of diamond films. When diamond films were synthesized on the WC substrate surface via the flame combustion, the amount of diamond paste with diamond seed particles affected the surface morphology and surface roughness of the synthesized diamond films. Furthermore, to investigate the reason for this result, generation of nuclei on the substrate in the initial stages of synthesis and diamond seed particles on the substrate surface after the seeding treatment were observed by scanning electron microscopy. The effect of diamond seed attachment processing on the diamond films synthesized by flame combustion was studied. The relationship between the surface roughness, number of diamond generation nuclei on the substrate in the initial stages of synthesis, number of diamond particles on the substrate after the diamond seeding process, and amount of diamond paste were confirmed.
Keywords: Diamond films; Flame combustion; Tungsten carbide substrate for cutting tool; Diamond seed particle; Surface roughness; Delamination.

1. Introduction

Owing to its excellent properties, such as high thermal conductivity, hardness, and wear resistance, diamond is utilized in the industry for the manufacture of cutting and polishing tools. Diamond films have long been considered as coating material for cutting tools [1-3]. Thus, diamond has been extensively studied as a coating material for cutting devices [4-7].

Recently, tungsten carbide (WC) has been used as a cutting tool in the machining industry and dental machining applications. WC is very hard and brittle and is prone to wear and fracture during cutting. Worn and failed tools have to be discarded, which causes resource depletion and environmental pollution. If diamond films can be directly synthesized on the WC surface and good adhesion can be achieved, surface improvement in terms of hardness and wear resistance, can be realized. A chemical vapor deposition (CVD) method in which diamond is deposited on a WC surface has been developed [4-7]. However, there were limitations such as low adhesive strength between the synthesized film and substrate surface, and the low density of diamond nuclei on the surface. Thus, it is difficult to synthesize diamond films on WC surfaces. Moreover, the experimental equipment utilized in the CVD method is bulky, and the speed of synthesis is very slow.

The flame combustion method enables the synthesis of diamond using acetylene-oxygen gas (C_2H_2/O_2) flame combustion in ambient air [8][9]. It has various advantages over other methods, such as high synthesis speed, safety, and low cost of equipment, which are desirable in the industry. However, to date, the factors affecting diamond synthesis are unknown and no precise control of this method has been established. Moreover, during cooling, most diamond films synthesized by the flame combustion method delaminate because of thermal stress. We have previously synthesized diamond films on molybdenum (Mo) substrates using the flame combustion method [10-12]. We have also synthesized diamond films on a Ti substrate for dental implants using the flame combustion method [13]. In a previous report, diamond films were synthesized on WC substrates via flame combustion [14-16]. However, the synthesis of diamond films on WC substrates is difficult. Therefore, to synthesize diamond films and prevent film delamination, conditions for synthesis on WC substrates have been proposed.

To obtain high-quality diamond films and achieve good adhesion on WC substrates, diamond films were synthesized by flame combustion using a mixture of acetylene and oxygen gases. However, the surface roughness of most of the diamond films synthesized by this method increased, and it was necessary to reduce this roughness. Considering the roughness accuracy of the workpiece surface during cutting, and the performance of the cutting tool, a smaller surface roughness of the diamond films synthesized is desirable. As previously indicated, pretreatments on the substrate surface affect the synthesis. Hence, chemical processing was performed as pretreatment to prevent the delamination. Furthermore, diamond seed particles of approximately 0.25 μm diameter were dispersed in acetone as growth nuclei for the diamond synthesis. The WC substrate was then added, and seed attachment processing was performed for 30 min using an ultrasonic syringe. In this study, to reduce the surface roughness, the amount of diamond paste with diamond seed particles as generation nuclei for the diamond seed attachment processing of diamond films was carefully varied. When diamond films were synthesized on the WC substrate surface via flame combustion, the amount of diamond paste with diamond seed particles affected the surface morphology and surface roughness of the synthesized diamond films. Furthermore, to investigate the reason for these results, generation of nuclei on the substrate in the initial stages of synthesis and diamond seed particles on the substrate surface after the seeding treatment were observed by scanning electron microscopy, and the effect of diamond seed attachment processing on the diamond films synthesized by flame combustion was studied. Moreover, the relationship between the surface roughness, number of generated diamond nuclei on the substrate in the initial stages of synthesis, number of diamond particles on the substrate after the diamond seeding process, and amount of diamond paste were confirmed.

2. Experimental details

2.1 Substrate

Tungsten carbide (WC) was used as a substrate for diamond synthesis. The substrate was a disk of diameter 10 mm and thickness 3 mm.

2.2 Experimental equipment

The experimental setup is illustrated in Figure 1. A 100 × 100 × 55 mm^3 rectangular copper box was used for the cooling. Cooling water was poured into the box, and the film surface temperature was kept constant at 1273 or 1223 K. A noncontact infrared radiation thermometer was used to measure the film surface temperature during synthesis. As a support for cooling, a tungsten (W) rod, of diameter 10 mm, was set vertically at the center of the box and fixed to a table using a flange. The WC substrate was then attached to this rod. For efficient cooling, a thermally conductive Ag paste was applied between the WC substrate and the rod. Subsequently, they were then glued together in a furnace at 473 K.

A cooling box was placed on the stage. Because it was capable of moving vertically, the distance from the cooling-water side to the film surface was changed, and the film surface temperature was controlled. A stepping motor was set on the stage and was controlled using a stage controller.

Acetylene and oxygen gases were used as fuels for the synthesis. A burner was used for welding. Mixed gas was introduced into the burner and combusted. The exit diameter of the burner was 1 mm. In addition, a mass flow controller which could precisely control the gas flow rate and digitally display the flow quantity was utilized as the gas flow meter.

2.3 Synthesis conditions

In this experiment, the film surface temperature was changed twice during synthesis [14-16]. The first step of the method was performed at 1273 K to achieve high bonding strength. The second step was performed at 1223 K to ensure that a good diamond phase can be synthesized.

The synthesis conditions are listed in Table 1. These conditions have been determined and reported previously [14-16], and are believed to be the optimum conditions for preventing delamination during the synthesis of diamond films. The ratio of the oxygen flow rate (F_o = 63.8 cm^3/s) to acetylene flow rate (F_a = 70.9 cm^3/s) was set to $R_f = F_o/F_a = 0.90$, because delamination-free crystallite growth could be realized at $R_f = 0.90$ [14-16].

An outline of flame combustion is illustrated in Figure 2. Flame combustion comprises an inner cone, acetylene feather, and outer luminous layer. Diamond was synthesized using acetylene feathers. The distance *d* of the flame's inner cone from the WC substrate surface is indicated in the figure. During the synthesis, the diamond film synthesis and delamination were affected when the distance was altered, because there was a change in the acetylene feather area. We confirmed that delamination at d = 7.0 mm during diamond film synthesis could be effectively prevented [14-16]. Therefore, diamond films were synthesized at d = 7.0 mm. The processing time for each of the two steps in the method used was set to 1200 s, and the total synthesis time for both steps was set to 2400 s [14-16]. The average thickness of the synthesized films was 30 μm/h.

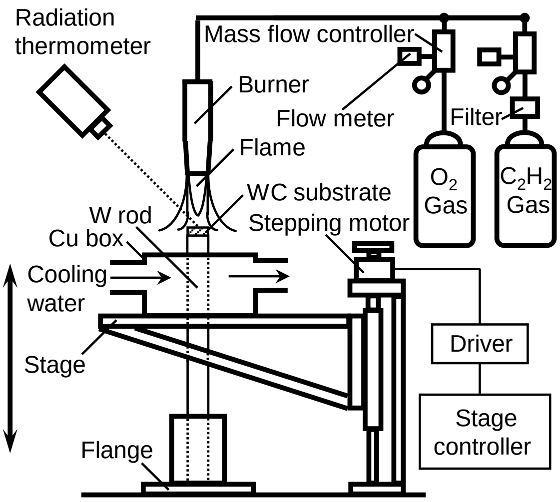


Figure 1. Experimental setup for synthesizing diamond film by acetylene-oxygen flame combustion.

Table 1. Conditions for diamond syntheses.

Reaction gas	$C_2H_2 + O_2$
Inner cone-to-substrate distances	7.0 [mm]
Pure C_2H_2 Flow rate, F_a	70.9 [cm^3/s]
O_2 Flow rate, F_o	63.8 [cm^3/s]
Flow ratio, $R_f = F_o / F_a$	0.90

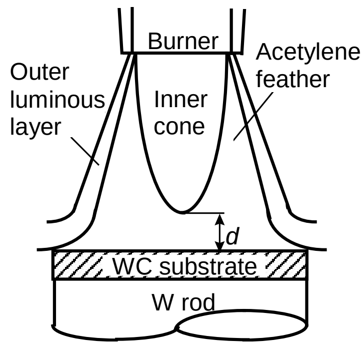


Figure 2. Outline of flame combustion.

2.4 Pretreatment of the WC substrate

It has been pointed out [14-16] that the surface roughness caused by pretreatments on the substrate surface causes delamination. Therefore, diamond films should be synthesized on the pretreated substrate surfaces.

Chemical processing was performed as a pretreatment to prevent delamination. The WC substrate was pretreated via chemical etching to roughen its surface [4][5]. The substrate was etched in an ultrasonic bath using Murakami's reagent ($K_3[Fe(CN)_6]$: 10 g; KOH: 10 g in 100 ml water). The treatment period was 10 min [4][5][14-16]. After the WC substrate was pretreated with Murakami's reagent, another process was performed using an acid solution of hydrogen peroxide (H_2SO_4: 3 ml + H_2O_2: 88 ml) to remove cobalt (Co) from the WC substrate surface. This is because WC contains Co as a binder, and the Co present on the substrate surface negatively affects the nucleation of diamond. Co functions as a catalyst for the formation of graphite and other non-diamond carbons [1]. Thus, the adhesive strength between the film and the substrate was very poor. To obtain good adhesion, Co was removed. The WC substrate used in this experiment contains 5-7 wt. % Co binder. The treatment period was 10 s [4][5][14-16].

Furthermore, diamond seed particles of approximately 0.25 μm diameter were dispersed in acetone as growth nuclei for the diamond synthesis. The WC substrate was then added, and seed attachment processing was performed for 30 min using an ultrasonic syringe. The amount of diamond paste with the diamond seed particles in acetone as generation nuclei was carefully varied for the diamond seed attachment processing of the diamond films. The amounts used were 2.50, 5.00, 7.50×10^{-3} g/cm^3. The pretreatment conditions are presented in Table 2.

Table 2. Conditions for amount of diamond paste with the diamond seed particles in acetone.

	Case A	Case B	Case C
Diamond paste [g] /Acetone [cm^3]	2.50×10^{-3}	5.00×10^{-3}	7.50×10^{-3}

3. Results and discussion

3.1 Delamination of synthesized films

Delamination of the synthesized films was completely prevented in all cases. Delamination was prevented simply by the pretreatment conditions and the amount of diamond paste with the diamond seed particles. The films were synthesized under the previously determined optimal conditions [14-16] to prevent delamination. We observed that the amount of diamond paste with diamond seed particles influenced the synthesized diamond films.

3.2 Investigation of synthesized films

The films synthesized under various pretreatment conditions were analyzed by scanning electron microscopy (SEM, JEOL JSM-5800) and X-ray diffraction (XRD, Rigaku RINT-2200V). The SEM images of the films synthesized for Cases A, B, and C are illustrated in Figures 3, 5, and 7, respectively. The SEM images show that the synthesized crystallites had a nearly uniform size and high density. The XRD patterns for Cases A, B, and C are illustrated in Figures 4, 6, and 8, respectively, where the peaks indicating the existence of diamond and the WC substrate were confirmed. Peaks indicating the existence of the diamond (111) and (220) surfaces were also confirmed. From the SEM images and XRD patterns, it can be observed that the diamond crystallites were synthesized. From the SEM results, the synthesized crystallites of the diamond films in each case indicated a uniform and high density. The synthesized crystallites became smaller as the amount of diamond paste with diamond seed particles in acetone increased. It was found that the surface condition of the synthesized films obtained by changing the amount of diamond paste used in the seeding process of diamonds on the WC substrate changed and that the change in the amount of diamond paste had a significant effect on the surface of the synthesized films. These changes in the amount of diamond paste are considered to have caused the changes in the state of the diamond particles attached to the substrate surface by the diamond seeding process and their initial nucleation state.

In each case, the amount of diamond paste used in the seeding process was varied to synthesize the diamond films on the WC substrates. Therefore, the synthesized films were analyzed by scanning white light interferometry (SWLI, Zygo New View6K), and the surface roughness *R*a (arithmetical mean deviation of the assessed profile) of the synthesized films was measured. The relationship between the measured surface roughness *R*a and the amount of diamond paste is illustrated in Figure 9. The error bars in Figure 9 illustrate the slight variation in the surface roughness, and the standard deviation is indicated. From the results, it can be confirmed that the mean value of the measured surface roughness changed in each case, and the measured surface roughness decreased as the amount of diamond paste increased. The results showed that the surface roughness of the synthesized diamond films was affected by the change in the amount of diamond paste. This is thought to be due to the change in the amount of diamond particles attached to the substrate as the amount of diamond paste was varied and the seeding process was performed. Here, if the amount of diamond paste is small, in Case A, the number of diamond particles attached to the substrate is small, the number of nuclei produced is small, and the size of the nuclei is large. In Case B, the amount of diamond paste was greater than that in Case A, the number of diamond particles attached to the substrate was greater than that in Case A, and the number of nuclei produced was greater. This is thought to have resulted in lower surface roughness. In Case C, the amount of diamond paste was greater than that in Case B, the number of diamond particles attached to the substrate was greater than that in Case B, the number of nuclei produced was greater, and the size of the nuclei was smaller for the same reason as in Case B. The surface roughness was considered to be the lowest. The results show that it is possible to change the surface roughness of the synthesized diamond films by varying the amount of diamond paste when synthesizing the diamond film.

Therefore, to investigate whether the initial nucleation is affected by the change in the amount of diamond paste, we focused on the initial diamond nucleation in the first synthesis stage. In each case, the amount of diamond paste with the diamond seed particles was varied, as shown in Table 2, and the state of diamond nucleation in the initial stages of synthesis was observed using SEM (JEOL JSM-7800F). From the obtained results, we could determine the effect of varying the amount of diamond paste during the seeding process on diamond nucleation during the synthesis.

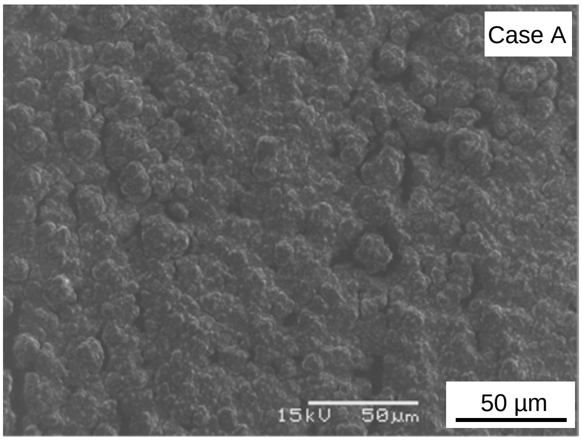


Figure 3. SEM image of the synthesized diamond film for Case A.

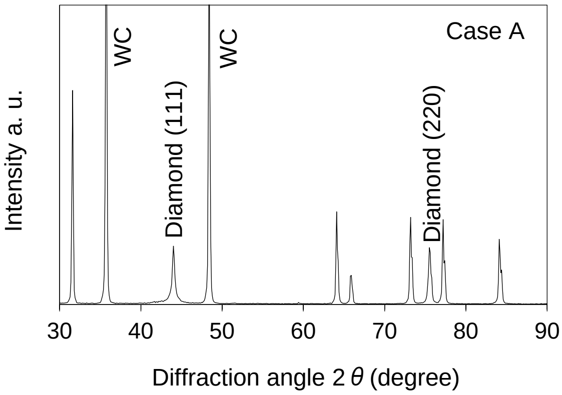


Figure 4. XRD patterns of the synthesized diamond film for Case A.

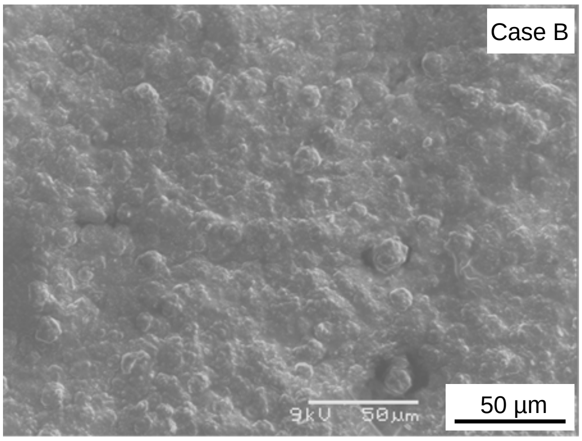


Figure 5. SEM image of the synthesized diamond film for Case B.

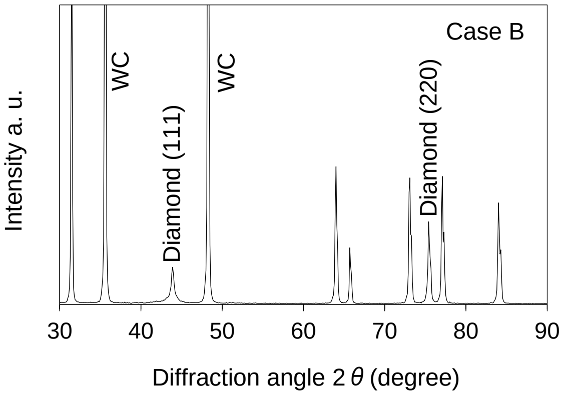


Figure 6. XRD patterns of the synthesized diamond film for Case B.

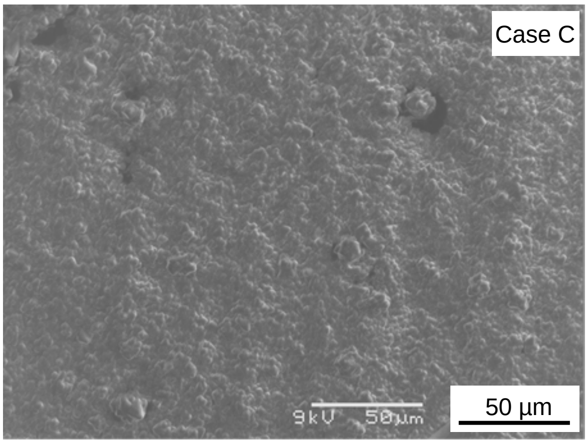


Figure 7. SEM image of the synthesized diamond film for Case C.

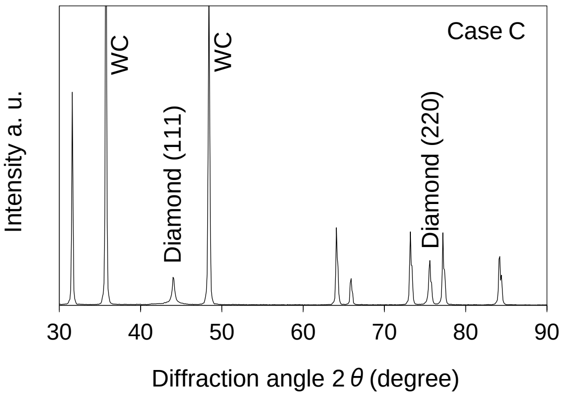


Figure 8. XRD patterns of the synthesized diamond film for Case C.

Observations of the substrate surfaces were made after the first 60 s of the synthesis, in which the amount of diamond paste used for seeding was varied in each case. The SEM images of the substrate surfaces after the first 60 s of synthesis for Cases A, B, and C are shown in Figures 10, 11, and 12, respectively. These figures show that nucleation occurred on the WC substrate surface in each case when the amount of diamond paste during the seeding process was varied, and diamond synthesis was performed. From Figure 10, it can be observed that the number of nuclei nucleated in Case A is small, and the size of the nuclei becomes large. Figure 11 shows that the number of nuclei nucleated in Case B was larger than that in Case A. The size of the nuclei is smaller than that in Case A.

From Figure 12, in Case C, the number of nucleated nuclei increased and the number was larger than that in Case B. The size of the nuclei became smaller than that in Case B when the amount of diamond paste was increased. These results indicate show that the state of nucleation on the substrate changes when the amount of diamond paste is varied. The relationship between the measured number of particles nucleated on the substrate after 60 s of synthesis and the amount of diamond paste used is illustrated in Figure 13. The error bars in Figure 13 are due to the slight variation in the number of particles nucleated on the substrate, and the standard deviation is indicated. From Figure 13, it can be confirmed that the mean value of the measured number of nucleated particles on the substrate changes in each case, and the measured number of nucleated particles on the substrate increases as the amount of diamond paste increases. The size of the nuclei on the substrate decreases as the amount of diamond paste increases. This is thought to be because the number of diamond particles on the WC substrate also increased as the amount of diamond paste increased. The results showed that the nucleation was affected by the change in the amount of diamond paste.

The results show that the amount of nucleation is affected when the amount of diamond paste is varied, and that the amount of nucleation on the substrate also increases with the amount of diamond paste, and the size of nuclei is small on the substrate as the amount of diamond paste increases; thus, the surface roughness of the synthesized film was observed to have been affected.

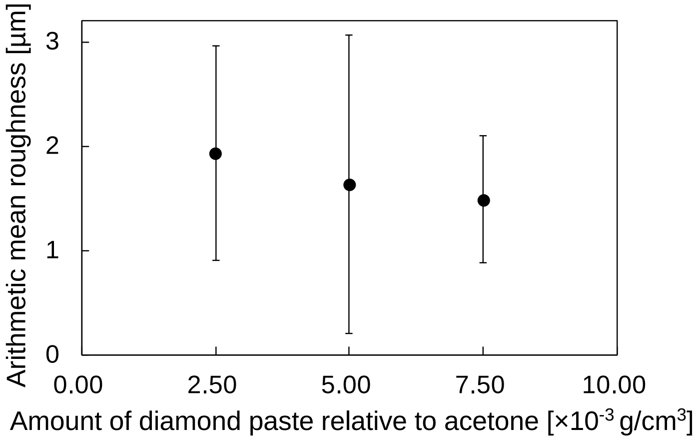
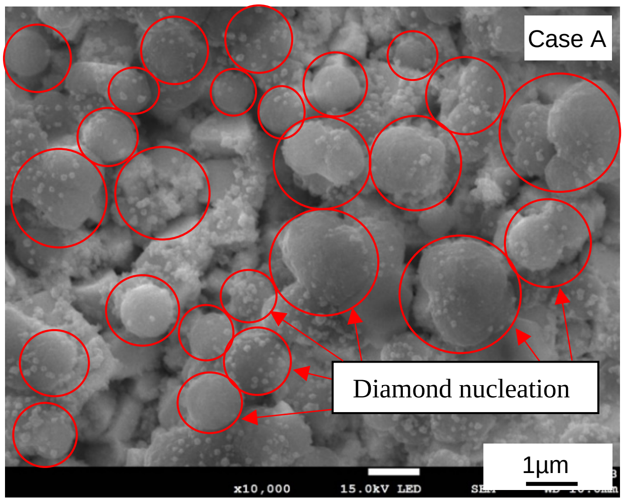
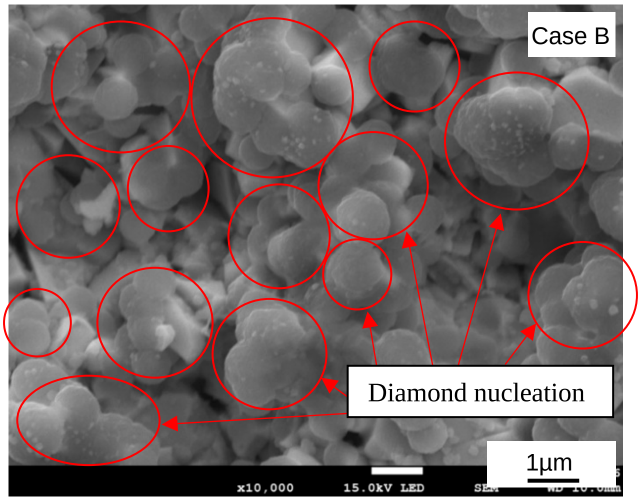


Figure 9. Results of surface roughness of synthesized diamond films on WC substrates for each case.

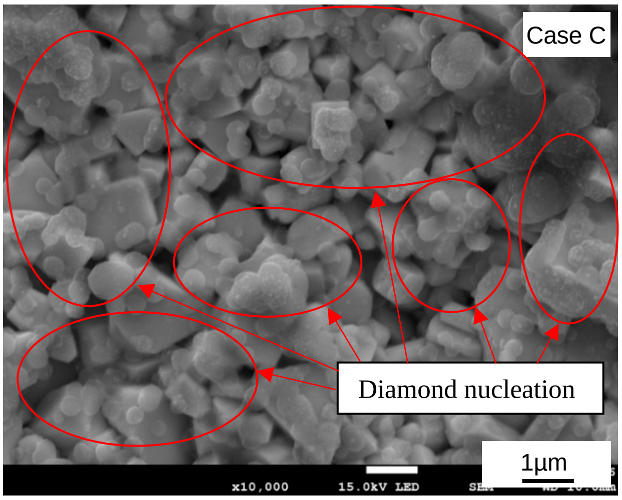


Figures 10. SEM image of the substrate surfaces of the synthesized films after the first 60 s for Case A.

The amount of diamond paste used in the diamond seeding process was varied to affect diamond nucleation after the first 60 s of the synthesis. This is thought to be due to the state of the diamond particles attached to the substrate surface during the diamond seeding process. Therefore, to investigate whether the diamond particles attached to the WC substrate were affected by the change in the amount of diamond paste, we focused on the diamond particles attached to the WC substrate after the diamond seeding process. In each case, the amount of diamond paste with the diamond seed particles was varied, as shown in Table 2, and the state of the diamond particles adhering to the substrate was observed using SEM (JEOL JSM-7800F). Based on the obtained results, we studied the effects of varying the amount of diamond paste during the seeding process on the diamond particles attached to the WC substrate.



Figures 11. SEM image of the substrate surfaces of the synthesized films after the first 60 s for Case B.



Figures 12. SEM image of the substrate surfaces of the synthesized films after the first 60 s for Case C.

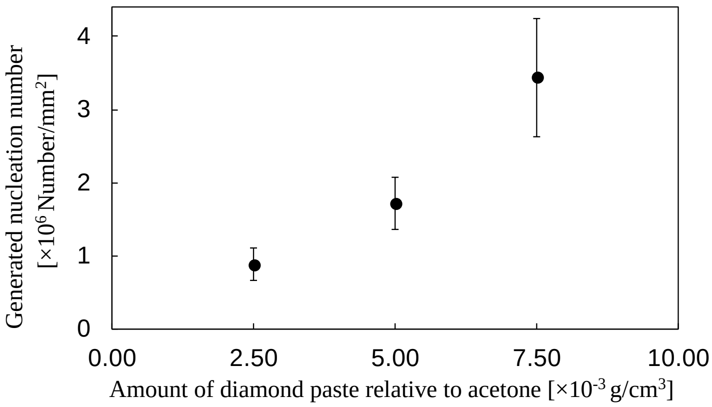
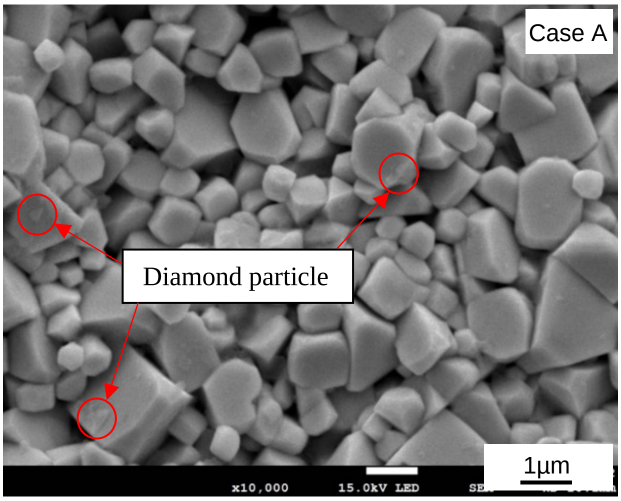
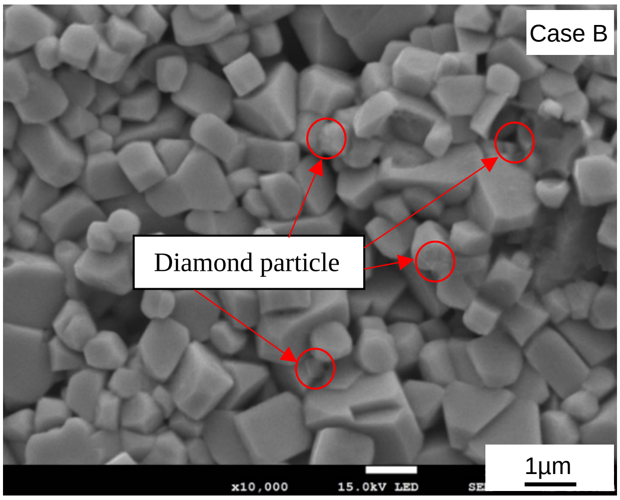


Figure 13. Results of measuring the number of particles nucleated on the substrate after 60 s of synthesis for each case.

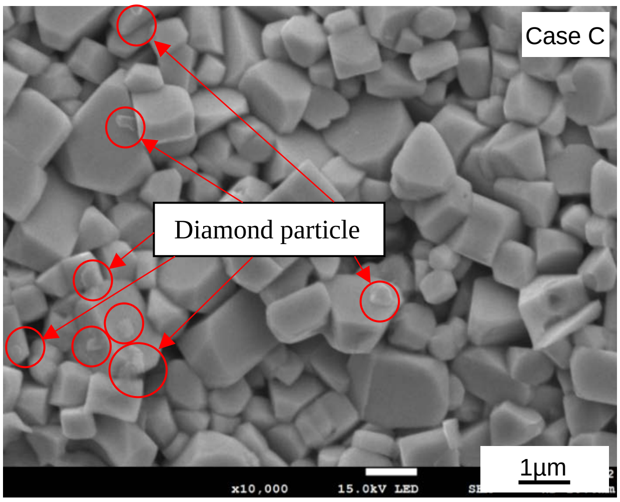
Observations of the substrate surfaces were made after the diamond seeding process, in which the amount of diamond paste used for seeding was varied in each case. SEM images of the substrate surface after the diamond seeding process for Case A, B, and C are shown in Figures 14, 15, and 16, respectively. The figures show that the diamond particles adhered to the substrate in each case, and that the diamond particles on the substrate increased with the amount of diamond paste. The relationship between the measured number of diamond particles on the substrate and the amount of diamond paste is illustrated in Figure 17. The error bars in Figure 17 are due to the slight variation in the number of diamond particles on the substrate, and the standard deviation is indicated. From Figure 17, it can be confirmed that the mean value of the measured number of diamond particles on the substrate changed in each case, and the measured number of diamond particles on the substrate increased with the amount of diamond paste. The results showed that the number of diamond particles attached to the substrate surface was affected by the change in the amount of diamond paste.



Figures 14. SEM image of the substrate surface after seeding treatment for Case A.



Figures 15. SEM image of the substrate surface after seeding treatment for Case B.



Figures 16. SEM image of the substrate surface after seeding treatment for Case C.

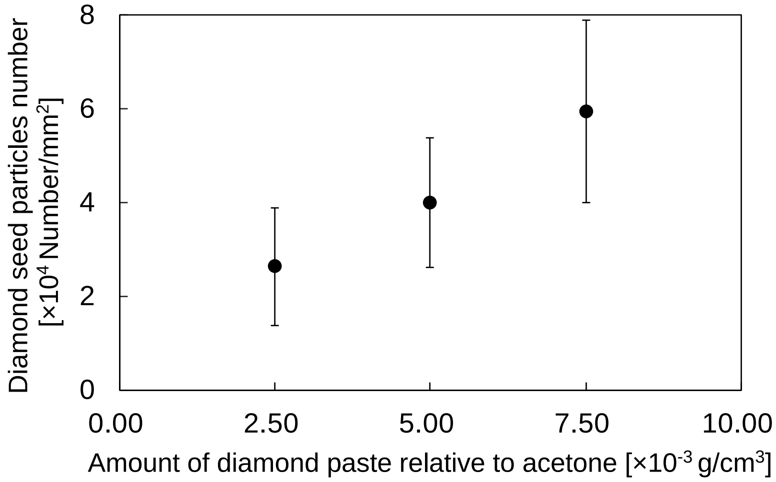


Figure 17. The results of the number of particles after seeding treatment for each case.

4. Conclusions

In this study, the amount of diamond paste with diamond seed particles as generation nuclei was carefully varied for the diamond seed attachment processing of the diamond films (2.50, 5.00, 7.50×10^{-3} g/cm^3) to reduce surface roughness.

The delamination of the synthesized films with varying amounts of diamond paste and the diamond seed particles in acetone was completely prevented. Delamination was prevented simply by the pretreatment conditions and the amount of diamond paste with the diamond seed particles. We observed that the amount of diamond paste with diamond seed particles affected the synthesized diamond films.

The synthesized crystallites became smaller as the amount of diamond paste with diamond seed particles in acetone increased. It was also confirmed that the mean value of the measured surface roughness changes in each case, and the measured surface roughness (the arithmetic mean roughness (*R*a)) decreased as the amount of diamond paste increased. The results showed that the surface roughness of the synthesized diamond films was affected by the change in the amount of diamond paste.

In addition, it can be concluded that the mean value of the measured number of nucleated particles on the substrate after the first 60 s of the synthesis changed in each case, and the measured number of nucleated particles and diamond particles on the substrate increased with the amount of diamond paste. The size of the nuclei on the substrate decreased the amount of diamond paste increased.

The mean value of the measured number of diamond particles on the substrate after the diamond seeding process changed in each case, and the measured number of diamond particles on the substrate increased with the increase in the amount of diamond paste.

The results showed that the amount of nucleation and diamond particles attached to the substrate surface was affected by the change in the amount of diamond paste.

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