

MULTI-SHAPED AND HYBRID DIAMOND PARTICLES BY VAPOR PHASE METHOD

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Recently low pressure vapor phase methods have been remarked, which permit control of the shapes of particles and the synthesis of thin diamond films and coatings. We employed the hot-filament method and developed several ways to control particle morphology by nucleation and growth conditions and produced 3 types of diamond particles: diamond automorphic, mirror-ball shaped, and multi-tetrahedron projection. The first one is produced in submicrons to about 250 micron size. The last two, i.e. multi-shaped particles, can be obtained in the submicron to scores of microns range and in sharp size distributions. We have also produced diamond-ceramic hybrid particles in two forms: isolated diamond grains and thick diamond layer coatings. Hybrid particles as large as a few hundreds microns are relatively easily produced. The particles were investigated for morphology, bonding structure, and preferred orientation. They were all characterized by sp^3 diamond structure, but some of them contained a small amount of i-carbon. The unique morphologies of the two multi-shaped particles are thought to be characteristic of the vapor phase methods, and it has become clear that there is a slight degree of preferred crystallite orientation. The potential of the new diamond particles for precision machining is briefly discussed.

1. Introduction

Synthetic diamond has been produced for industrial uses by two methods, static ultra-high pressure and high temperature with catalysis by General Electric, and direct transformation of graphite to polycrystalline diamond using shock wave impaction by Du Pont.

Recently, low pressure-vapor phase methods have been developed, which were started by Derjaguin¹⁾ and confirmed by Matsumoto²⁾. Contrary to the ultra-high pressure and high temperature method, vapor phase methods can be used to control the shapes of particles and to synthesize thin diamond films and coatings³⁾.

In vapor phase methods, hot-filament, MW and RF plasma and DC arc methods have been developed. Although researches on the vapor phase methods in general are mainly concerned with thin films and coatings, we have been investigating synthetic methods for mass production of diamond particles.

Using the hot-filament method^{4),5)} we have developed several ways to control diamond particle morphology by nucleation and growth conditions,

resulting in large single crystal-like and multi-shaped particles. We have also produced diamond-ceramic hybrid particles in a continuous process.

2. Synthetic process

In the carbon phase diagram, the synthetic regions of vapor phase methods are in the meta-stable state of diamond, while in those of the traditional, ultra-high pressure and high temperature methods the diamond phase is stable. The synthetic range of vapor phase methods is considered to be at less than 1 atmosphere pressure and temperatures of around 1000°C. A continuous supply of H_2 and hydrocarbons is fed to the special reaction region.

Using hot-filament methods, we have succeeded in controlling the diamond particle morphology by nucleation with specific materials and growth conditions. Furthermore, diamond-ceramic hybrid particles have been developed with deposition of diamond on ceramics such as SiC particles as a depositing substance in a continuous process. According to the deposited diamond crystallite morphologies, two types of hybrid particles, iso-

projections. Both multi-shaped particles can be obtained in the size range of submicrons to scores of microns and in a sharp size distribution.

The SEM micrographs of diamond-ceramic hybrid particles produced with SiC particles in a kind of fluidized bed are shown in Fig. 3(a)–(c). In Fig. 3(a), the automorphic diamond particles deposited separately on SiC are shown. Figure 3(b) shows a type of diamond hybrid particles produced with thick diamond crystalline layers on SiC particles. Figure 3(c) shows an enlarged micrograph of the hybrid particles coated with a diamond layer.

The Raman spectra of the automorphic diamond and multi-shaped particles are shown in Fig. 4; each spectrum has a sharp diamond peak at 1333 cm^{-1} . The low broad peaks of i-carbon content are observed in the multi-shaped mirror ball and multi-tetrahedron particles, but very little in the diamond automorphic particles. Therefore, the i-carbon phase might correspond to the growth mechanism of multi-shaped particles.

Figure 5 shows the Raman spectra of two hybrid particles. Two spectra indicate almost nothing except 1333 cm^{-1} diamond peaks, which means that both hybrid particles have high quality diamond crystals and diamond crystalline layers.

In Fig. 6, X-ray diffraction analysis on the single

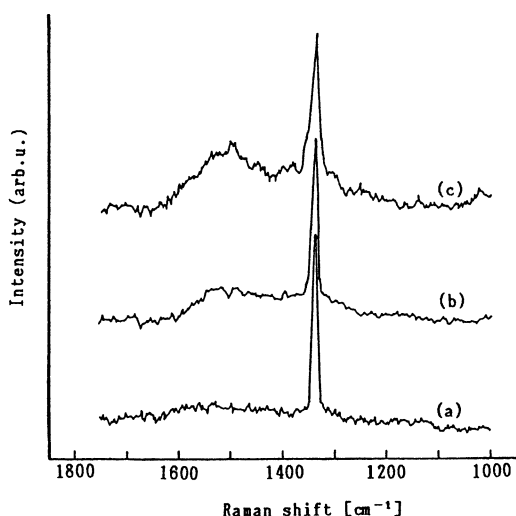


Fig. 4. Raman spectra of diamond particles. (a) Single crystal like. (b) Mirror ball-shaped. (c) Multi-tetrahedral projection.

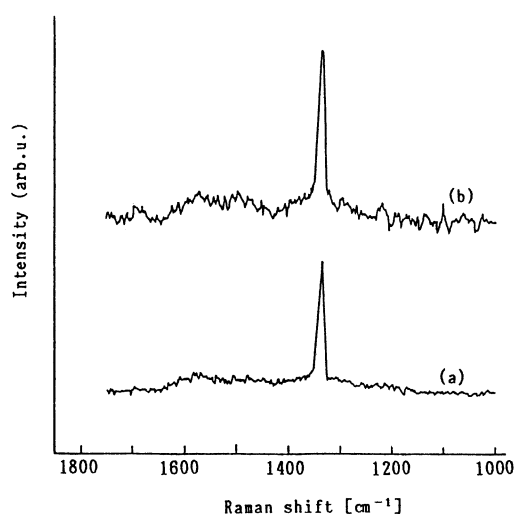


Fig. 5. Raman spectra of hybrid particles. (a) Isolated diamond particles. (b) Thick diamond crystalline layer.

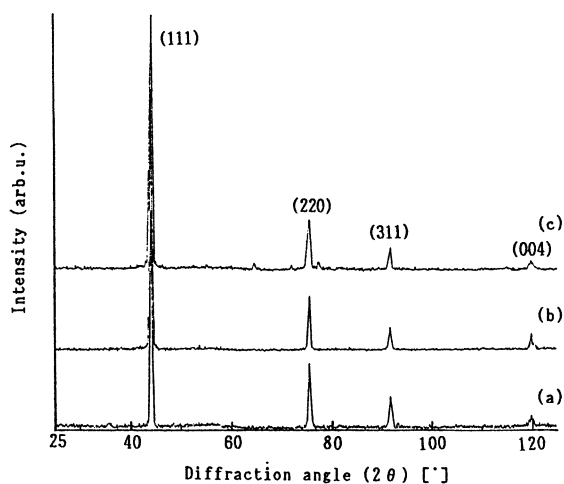


Fig. 6. X-ray diffraction patterns of single crystal like and multi-shaped particles. (a) Single crystal like. (b) Mirror ball-shaped. (c) Multi-tetrahedral projection.

crystal-like and multi-shaped particles are shown; relative peak-ratios based on (111) peak height are shown in Table I, with reference to ASTM values. On the single crystal-like particles, the relative peak height ratios are very close to those of natural diamond, except that the (220) peak is a little higher than the reference. The diffraction analysis on the multi-shaped particles shows a little bit of (100) preferred orientation for the mirror ball-

Table 1. The relative peak height ratio of diamond particles

	Single crystal like		Mirror ball-shaped		Multi-tetrahedral projection		ASTM
	P height	I/I_0	P	I/I_0	P	I/I_0	I/I_0
(111)	70.0	100.0	83.5	100.0	82.0	100.0	100
(220)	21.5	30.7	17.7	21.2	16.7	20.4	27
(311)	11.0	15.7	8.0	9.6	7.9	9.6	16
(004)	5.0	7.1	6.3	7.5	4.0	4.9	7

shaped particles and some degree of (111) preferred orientation for the multi-tetrahedral projection ones. Both preferred orientations of the multi-shaped particles are not as high as expected from their particle morphologies.

4. Applications

Cubo-octahedron-like particles of 100 microns order sizes have been produced by a vapor phase method, and can be applicable as conventional abrasive grains.

The multi-shaped diamond particles are polycrystalline, which has an edge-forming effect through small chipping of particle projections at abrasive loading, so that they might have high performance as abrasive and lapping agents. Furthermore, they are expected to bind strongly without any specific surface treatments, due to their unique projections in various matrices.

Hybrid diamond particles as large as a few hundreds microns in size are relatively easily produced and have a stiff and thick polycrystalline diamond layer. As a substitute for diamond grains, either natural or synthetic, the hybrid diamond particles can be used to develop a new application area in the machining field.

5. Conclusion

The shapes of natural diamond particles and high pressure synthetics were very limited, but multi-shaped and hybrid diamond particles have been available by vapor phase methods in our studies. Compared to the conventional ultra-high pressure and high temperature method, vapor phase methods use relatively simple apparatus which can be operated in less complicated ways and continuous processes.

Although many things, especially in growth mechanisms, are still ambiguous and many studies must be done, in the near future the diamond particles grown by vapor phase methods, "new diamonds", will be successfully used in precision machining fields.

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