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SPECIFICATION

Narrow size-ranged single crystalline minute diamond particles and method for the production thereof



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5 *Technical Field*

This invention relates to narrow size-ranged single crystalline minute diamond particles and, in particular, to diamond abrasive powder especially adapted for the super precision machining of high hardness substances and a composite body such as a thin-film magnetic head blank that is made up of materials different in hardness.

10 *Technical Background*

With the recent advance in machining techniques, the needs for diamond abrasives are shifting to increasingly finer particles, such that submicron sizes, or particles with a diameter smaller than one micrometer, find more and more uses in many sectors of the industries. Also demands appear to rise higher year by year for the properties and, in particular, size distribution of those minute particles.

Diamond particles are generally produced by converting non-diamond carbon in a static ultrahigh pressure process to single crystals of diamond, which then are crushed and sorted by size. With inherent difficulties in crushing-and-sorting processes, this technique, however, cannot provide particles smaller than something around a nominal size of 0-0.1 μm or a D50 particle size of 0.12 μm or so by MICROTRAC UPA evaluation.

On the other hand some techniques have been also established on a commercial scale, whereby graphite or an explosive chemical is converted to diamond under shock wave or dynamic compression. The former product, converted from graphite, is called Dupont diamond, while the latter, which is prepared by using explosive as a carbon source, is known as cluster diamond or ultrafine diamond. Both type diamonds are

widely employed as an abrasive material in precision machining applications.

As well known, such products from dynamical compression processes generally consist of primary particles with a diameter of a few to tens of nanometers, which are observed to collect or join together to form polycrystalline, secondary particles that
5 have an apparent diameter (particle size) of hundreds of nanometers to a few micrometers.

The Dupont diamond is commercially available, similarly to the static ultrahigh pressure compression product, down to secondary particle sizes of something around a nominal size of 0-0.1 μm or a MICROTRAC D50 particle size of 0.12 μm or so.

10 The cluster diamond described above is available as aggregate particles with an apparent particle size of a few micrometers, which can be reduced by intense oxidation to primary particles with a diameter of, it is said, 5 to 10 nm.

In those circumstances the smallest particle size available of single crystalline diamond for abrasive uses appears to be 0-0.1 μm (100 nm) by nominal size
15 designation or a D50 average size of 0.12 μm (120 nm) by MICROTRAC UPA evaluation. No sizes have been commercially available between 0.01 and 0.12 μm , in particular, for this type of diamond, to meet effectively the increasingly complicating needs in the high precision machining processes.

Moreover, while 0.25 μm and smaller size diamond powders may be available,
20 they are produced by collecting to contain the whole undersize particles present, as indicated in a designation such as 0-0.25 or 0-1/8. Besides increasing the size range, the undersize comprises very minute particles to a zero size, which not only are useless for the machining but also can even affect adversely. The content of such minute fraction results in a lower apparent D50 size evaluation for the product than the latter
25 performs actually.

On the other hand, the recent advancement in demands for the performance or functions of optic, electronic, and precision machine parts etc. require the use of a

variety of materials, from metals to ceramics to glasses to plastics. The manufacture of those parts increasingly involves the machining of composite bodies made of several materials different in hardness. Thin film magnetic heads (blanks), for example, consists of a base of, for example, altic ($\text{Al}_2\text{O}_3\text{-TiC}$) protective-insulating film of ceramic such as alumina (Al_2O_3), and magnetic film of permalloy (Fe-Ni) or sendust (Fe-Al-Si), which is among favorite works for the abrasive process with the diamond powder of the invention.

The air bearing surfaces (ABS) of a magnetic head has been mainly machined with the polycrystalline diamond abrasives, produced under shock-wave compression. This abrasive product grinds, due to hardness difference of the head materials, metallic film in preference to the rest as being the softest of all, thus inevitably leaving unevenness or roughness on the worked surface.

This can cause a problem of pole tip recession (PTR): the pole tip, being the part made of metallic film, becomes more abraded and in the end comes to a position behind from the rest of air bearing surface that is made of ceramic material, thus causing an increase in magnetic gap between the medium and effective flight height.

The use of smaller nominal size diamond particles may be regarded as a possible solution for minimizing the level difference to occur within the surface because of the difference in hardness between the materials of a thin film magnetic head. However conventional abrasive particles (polycrystalline type diamond) comprise, besides the effectively performing fraction, a significant proportion of smaller particles that are limited in polishing performance. While those very minute particles do not effectively abrade the harder part of ceramic such as altic or alumina, they abrade the softer part, in particular, of metallic material such as permalloy or sendust.

In the case of the conventional diamond particles, while smaller size particles can somewhat decrease the pole tip recession, selective abrasion becomes more noticeable within the film of different metallic components than with larger nominal sizes. It may happen this way: As a thin film magnetic head blank is polished on a

plate (lapping plate) where slurry of abrasive particles is fed by dripping, smaller particles roll around between the head and plate, while the larger particles, or effective fraction, become fixed as being caught and partly embedded in the plate, in order to properly perform in the polishing process.

5 Another problem in the polishing of thin film magnetic head with conventional single crystalline diamonds is that there are some particles remaining stuck to the metallic film of the air-bearing surface. This must be minimized as far as possible as being a possible hazardous flaw: When mounted in a hard disk drive and operated, such diamond particles may come apart from the head while it flies. Some may land on
10 the disk to eventually cause a crush.

There is a tendency with conventional single crystalline diamond abrasives that the number of stuck particles increases as the abrasive nominal size decreases, so this type of abrasive could hardly be a solution for the suppression of both stuck particles and pole tip recession described above.

15 In such circumstances there has been a substantial need for a novel abrasive that could reduce effectively the PTR and number of particles stuck to the head metallic film, in order to achieve some improvement in storage density of a fixed disk.

Therefore one of the principal objects of the invention is to provide a closely sized single crystalline diamond particleabrasive, comprising little proportion of
20 harmful undersize particles, thus allowing a high precision machining of various hard substances.

Another object is to provide such type of diamond abrasive especially adapted for the machining of thin film magnetic head of composite body, which is made up of differently hard components. And it can achieve an improved quality and low-PTR
25 finished surface as a result of effective suppression of both selective abrasion of softer parts and stuck particles.

The inventors have found, and based this invention on, that: conventional single

crystalline diamond abrasives comprise a substantial proportion of very minute particles, or smaller-end size particles. Identified as the probable cause of the above described problems, a total or substantial elimination of such fraction in the course of preparation of the abrasive results in both a decreased pole tip recession and
5 suppressed stuck abrasive particles in the machining (polishing) of thin film magnetic head blanks.

Disclosure of the invention

As the one of the principal objects described above, the diamond particle abrasive of the invention, adapted for an high precision machining of common
10 materials, can be achieved by providing single crystalline diamond particles prepared under static ultrahigh pressure compression, micro pulverizing by crushing and sorting into submicron sizes. The particle sizes distribution is elaborated to such that the D50 size value equals to 120 nm or less and, preferably, 100 nm or less. The ratios of D10 and D90 values to D50 value are adjusted to be 50 % or more and 200 % or less,
15 respectively, said sizes being evaluated by means of MICROTRAC UPA size analyzer.

Next, the second diamond particle abrasive of the invention is especially adapted for the high precision machining of a composite work of differently hard components. It also is a sized loose mass of single crystalline diamond particles, and the size
20 distribution is so elaborated as to have a D50 average particle size d_{50} of 120nm or less and that the fraction of 0.7 time d_{50} or less is 15 % or less. Such evaluation and indication of each parameter and size distribution is based on the observation with a MICROTRAC UPA particle size analyzer.

The diamond powder can be obtained typically by subjecting single crystalline
25 diamond, converted under ultrahigh pressure compression, to micro crushing and precision sizing processes, the both processes are repeated until either d_{D50} of 120 nm or less and, preferably, 100 nm is achieved.

Brief Description of Drawing

Fig. 1 graphically shows the particle size analysis for first single crystalline minute diamond particles prepared in accordance with an example of the invention.

Fig. 2 graphically shows the particle size analysis for second single crystalline minute diamond particles prepared in accordance with an example of the invention.

In the figures the bars represent the size frequency or relative volume of each ranged size fraction relative to the whole sample, and the curve indicates the cumulative frequency.

Preferred Embodiment of Invention

For the micro crushing of the invention available are impact crushing with steel balls, such as ball milling and attrition. The precision sizing, on the other hand, may be based on elutriation by adjusting to optimize the flow rate of the medium. The removal of undersize minute particles can be promoted and an efficient process can be realized by using an upward flow rate twice to four times the theoretical data that is determined in accordance with Stokes' law.

It is preferable that diamond particles should be heated, in the course of sizing, to a temperature within a range of 800° to 1400° C, in order to adapt to the softer or lower hardness component of the work. Such heat treatment yields a thermal affected structure with decreased mechanical strength and further graphite or non-diamond carbon converted from the diamond partly in the surface. Thus when employed for machining, the deposit moderates the impact to the work at the moment of contact, so the occurrence of deep abrasion marks and stuck diamond particles is effectively suppressed. Further, the deposition of such carbon or graphite decreases the relative height of surface edge projections on most particles and thus the depth of resulting abrasion marks. The effect of non-graphite is noticeable when deposited at a weight ratio to the whole diamond of or over 0.5 %.

Example 1

2-6 μm nominal size single crystalline diamond particles (TOMEI DIAMOND IRM grade) were subjected to both micro crushing and precision sizing.

For the crushing process used was a steel ball-mill pot with both diameter and length of 250 mm. Loaded of 300 grams of the above said starting diamond powder along with 20 kg of 6 mm diameter steel balls, it was driven at 80 R.P.M. for 120 hours. The crushed powder was taken out of the pot and placed in 10 HCl-1 HNO₃ mixed acid solution, in order to remove by dissolution the iron ingredient, and then washed fully in water.

For the elutriation process an arrangement of serial connected tubes was used, both having a 20 cm-long straight cylindrical portion, and one having a cross section of 2500 cm² for the first step and the other, 5000 cm² for the second step. This system of tubes was loaded with 1 kg of the crushed diamond, and elutriation was operated while feeding 120 liters of ion-exchanged water at a rate of 25 cc per hour. As overflowing from the second step suspension was collected into a reservoir, to which hydrochloric acid was added to maintain a pH of 2.

The table below shows the particle sizes evaluated upon the elutriation for the steps by means of MICROTRAC UPA particle size analyzer.

It is seen that each mass of diamond particles collected from the first and second steps, as well as the outflow, has a narrow ranging size distribution as observed in terms of these parameters: the ratio D90/D50 being 156, 132 and 177 %, and the ratio D10/D50 being 60, 75 and 58 %, respectively.

Parameter	D10	D50	D90	D90/D50
first step	59	99	154	156%
second step	56	75	99	132
outflow	31	53	94	177

The particle size distribution is shown in Figs. 1 and 2, for the mass collected in the above example from the first step and outflow, respectively, as evaluated by means of MICROTRAC UPA particle size analyzer. Here the bars represent the frequency of the sizes within the given range in the evaluation, while the curve indicates the cumulative frequency, wherein frequency for each size point is accumulated.

Example 2

TOMEI DIAMOND MD100 (trade name) diamond powder was used as a starting material, which is an abrasive product prepared through elutriation and directed for precision machining processes.

10 This abrasive powder had a MICROTRAC size distribution such that the D50 value is at 103.9 nm, while there was an accumulation of 19.75 % as up to the 27th channel (72.3 nm), which corresponds to 70 % said D50 value. That is the starting powder comprised an approximately 20 % part of under 70 nm particle size fraction.

15 1 kg of such diamond powder was loaded in an elutriation system of the same arrangement as in example 1, and sorted while feeding ion-exchanged water at a rate of 0.5 cc per minute.

As re-sized by this process, the collected powder had a MICROTRAC D50 value of 107.4, which was practically the same as the average size of the starting powder. However the frequency accumulation at the 27th channel (72.3 nm) corresponding to 20 70 % d_{D50} value, was 11.07 %. That is the fraction of under 70 nm particle sizes was decreased to about 11 %.

The above said diamond was heat treated for the powders as before- and after this additional elutriation, by placing each powder on a porcelain boat, replacing the atmosphere with nitrogen and heating at a temperature of 1200° C for 3 hours.

25 Oil dissolvable slurry was prepared using the heat treated diamond powders, either with- (invention) or without the additional elutriation (for comparison purpose),

and then tested each in the lapping of an air bearing surface of thin film magnetic head blank.

The performance of each slurry was evaluated in terms of PTR value and number of particles stuck to the metallic film. In particular, a work of composite block was prepared from altic ($\text{Al}_2\text{O}_3\text{-TiC}$), alumina (Al_2O_3) and Permalloy (Fe-Ni) and sendust (Fe-Al-Si), in order to simulate the magnetic head and to evaluate the resulting level unevenness. Also the number of stuck particles was counted by SEM observation of the surface within the $5\text{ }\mu\text{m}$ sided square metallic film.

The PTR value was determined for the diamond powder of the invention as 2.355 angstrom, which is 52.2 % the value 4.464 angstrom for the conventional type.

The number of stuck particles was 3 for the abrasive of the invention, as compared to the conventional type, which counted 15.

Applicability to the Industry

The diamond particle abrasive of the invention has a unique narrow range of particle sizes at a D50 average particle size of 120 nm or less, while retaining the single crystalline structure, characteristic to the static ultrahigh pressure technique for the conversion. The product can be successfully employed, to the high precision machining of composite work materials and, in particular, low PTR machining of thin film magnetic head blanks comprising differently hard components, as well as common singly hard works.

Claims

1. Single crystalline submicron-size diamond particles converted from non-diamond carbon in a static ultrahigh-pressure process and crush-pulverized and sorted by size, having a D50 particle size of or less than 120 nm and a narrow particle size range
5 characterized by ratios of D10 and D90 particle sizes in relation to D50 particle size being 50% or more and 200% or less, respectively, said particles sizes being evaluated by means of MICROTRAC UPA particle size analyzer.
2. The diamond particles as claimed in claim 1, in which said D50 particle size is 100 nm or less.
- 10 3. A diamond abrasive powder comprising a loose mass of single crystalline diamond particles, a sample of which has a D50 average particle size (d_{D50}) of or less than 120 nm and a relative volume of $0.7 \times d_{D50}$ or less size particles being 15 % or less the whole sample, as evaluated by means of MICROTRAC UPA particle size analyzer.
4. The diamond abrasive powder as claimed in claim 3, in which said diamond
15 particles have a thermal affected structure as a result of a heat treatment and are covered with non-diamond carbon, which amounts 0.5 % by weight or more the mass of diamond particles.
5. The diamond abrasive powder as claimed in claim 4, in which said diamond particles have undergone a heat treatment at a process temperature of 800° to 1400° C.
- 20 6. A method for producing single crystalline submicron-size diamond particles, comprising: providing single crystalline diamonds prepared in a static ultrahigh pressure compression process, pulverizing by crushing to reduce in size and further precision sizing into powders of D50 average particle sizes of or less than 120 nm.
7. The method as claimed in claim 6, in which said D50 average particle size is 100
25 nm or less.

8. The method as claimed in claim 6, in which said crushing is carried out dynamically by ball milling or attrition with steel balls.
9. The method as claimed in claim 6, in which said precision sizing is carried out by elutriation.
- 5 10. The method as claimed in claim 6, in which said elutriation uses an upward water flow rate twice to four times a theoretical precipitation rate for the particles that is to be determined on the basis of Stokes' law.