ABRADERS, ABRASIVE PARTICLES AND METHODS FOR PRODUCING SAME

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ABSTRACT

Abraders are formed from encapsulated abrasive particles which are uniformly distributed in a matrix. Superior abraders may be formed by metal bonding such encapsulated abrasives with a metal matrix which forms a continuous phase in which the abrasive particles may be positioned. Where the abrader is formed from a mixture of the bonding metal and a single type of abrasive particle, the specific gravity of the abrasive particle may be adjusted to match more closely that of the metal. The encapsulated abrasive particle may form the primary abrasive together with a secondary abrasive which is not as hard as the primary abrasive and which may or may not be encapsulated with a metal.

Where a plurality of abrasive particles of differing specific gravity are used, one or the other or both may be adjusted in density by employing an encapsulating metal of suitable specific gravity.

Abrasive particles are improved in function as abrasives, in addition to having the specific gravity adjusted by encapsulating them with a metallic envelope; preferably the envelope is made of a pure metal in dendritic crystalline form. Desirably the abrasive substrate is placed in contraction by the envelope which is heat shrunk onto the abrasive substrate. The preferred method is to deposit the metal on the substrate at an elevated temperature by contacting a vapor of the metallic compound with the substrate particle under reducing conditions. The preferred primary abrasive is a diamond, and it is preferably etched before coating.

24 Claims, 12 Drawing Figures
ABRADERS, ABRASIVE PARTICLES AND METHODS FOR PRODUCING SAME

This invention relates to abraders formed of a plurality of different abrasive particles bonded in a continuous phase matrix.

Abrasive, grinding, cutting and earthboring tools, hereinafter referred to as abraders, have bound abrasive particles into an abrader structure, using a binder such as an organic polymer resin and, in some cases, metal, which acts as the matrix to hold the abrasive particles in the abrader structure.

In one form of the above structures, a plurality of different abrasive particles are employed. In addition to particles of high hardness values which act as the primary abraders, there is distributed in the continuous phase of the metal matrix a secondary abrasive of lower hardness value.

The purpose of the secondary abrasive particles is to wear away preferentially thus exposing new abrasive faces of the primary abrasive particles.

It is desirable in such structures that the primary abrasive and the secondary abrasive be uniformly distributed throughout the matrix. If the primary abrasive is not uniformly distributed, the abrader structure will not be uniformly worn away and the result will be that at wearing areas of high concentrations of primary abrasive the abrader wears away less than in the area of low primary abrasives concentration.

The accelerated erosion of the secondary abrasive particle and the accompanying local wearing away of the bonding matrix results in a larger loading on the areas of higher primary abrasive particle concentration since the abrader structure will ride up on these areas. The load being concentrated on these reduced areas causes an increased load per unit area on the localized pressure areas and on the underlying abrader structure, such as a saw blade on which the abrader structure may be mounted.

In some cases, this increased load may fracture the primary abrasive and cause it to be torn out of the matrix resulting in excessive wear.

In such cases, the cutting rate may not be uniform and it is necessary to either reduce the loading or the cutting rate.

We have been able to overcome to a larger measure these disadvantages by providing for a more uniform distribution in the matrix of the primary and if used of the secondary abrasive particles to obtain a controlled and substantially uniform spatial distribution of primary and if used of the secondary abrasive.

In such cases, it is possible to select a concentration of primary and if used of secondary abrasive to provide a suitable spacing between the particles to provide sufficient pore volume to give a desirable bond and a sufficient mass of matrix to hold the abrasive particles in position.

This invention provides for the aforementioned uniform distribution of the primary and secondary abrasive if used by first forming an intimate mixture of particles of the primary and secondary abrasive in which the particles are as closely as is practically feasible of substantially the same density. Additionally, the uniformity may also be reinforced by using all particles in the same mesh size range and using them in as narrow a mesh size range as is practically convenient.

In such case, by suitable mixing of the particles the probability of the presence of a given abrasive particle and of a given particle of the metal in any volume in the array of particles in the mixture will be substantially equal. A uniform dispersion of substantially uniform concentration of primary and secondary particles, if used, throughout the mix will result.

When the specific gravity of the primary particles differs from that of the secondary abrasive particles, we may encapsulate the particles with a metal so as to bring the resultant densities of all of the primary and secondary particles to as nearly the same density as is conveniently feasible, i.e., that all of the particles have substantially the same density.

Where the abrader structure is to be used as a cutter or abrader, for example in oil well drill bits or other boring, shaping tools or saws suitable, for example, in sawing concrete, masonry, rocks, ceramics, bricks, etc., we prefer to use abrasive materials, preferably those having hardness in excess of about 2,500 kg/mm² (Knoop or Vickers) and the harder the better. An additional useful criteria is that the abrasive material should have a melting or softening point in excess of the highest temperature reached in the process by which the abrader structure is formed, such as is described hereinafter.

We prefer to employ, because of their physical properties, such as hardness, melting point, chemical stability, and other physical properties, one of the following abrasive materials, preferring among them diamonds, either natural or synthetic. In addition to diamonds, we may use any one of the following abrasive particles shown in Table 1. The values reported in the table are taken from the available literature.

As described above, we wish to select as the primary abrasive, one having a substantially higher hardness value than that of the secondary abrasive particle.

Table 1 lists suitable materials from which may be chosen the primary and accompanying similar abrasives.

TABLE 1

<table>
<thead>
<tr>
<th>M.P. °C</th>
<th>Sp.G.</th>
<th>Percent Linear Coeff. of Expansion $\times 10^{-6}$ 0-1000° F.</th>
<th>Hardness kg/mm²</th>
<th>Knoop*</th>
<th>Vickers**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamonds (Synthetic or Natural)</td>
<td>2060</td>
<td>3.5</td>
<td>1.5</td>
<td>8000*</td>
<td></td>
</tr>
<tr>
<td>Aluminum Oxide (Al₂O₃)</td>
<td>2060</td>
<td>3.5-4</td>
<td>4.4</td>
<td>3000*</td>
<td></td>
</tr>
<tr>
<td>Cast Eutectic Tungsten Carbide (WC)</td>
<td>4800</td>
<td>15</td>
<td>4.8</td>
<td>3000*</td>
<td></td>
</tr>
<tr>
<td>Tungsten Mono Carbide (WC)</td>
<td>4800</td>
<td>15.8</td>
<td>2.7</td>
<td>1700-2400</td>
<td></td>
</tr>
</tbody>
</table>

* Knoop hardness is a measure of the hardness of a material, determined by the indentation caused by a diamond pyramid indenter under a specified load. Vickers hardness is another measure of hardness, determined by the indentation caused by a flat diamond pyramid indenter under a specified load.
The method of encapsulation where a nonmetallic matrix is to be employed, for example, where an organic polymer resin is employed we may deposit the metal of higher specific gravity in any conventional method, such as electrochemical or electrolytic methods and conventional handbooks will list such metals. Where, however, we wish to employ the matrix as the matrix and apply the metal in molten condition to the mixed particles, we prefer to use metals as the envelope having a suitably high melting point. The densities of the several particles more closely to the same value.

The total weight of the particles is increased and as the increase in volume of the particles is the less the greater is the density of the envelope and vice versa. Since the metal envelope is chosen so that the specific gravity of the metal envelope be greater or less than that of the underlying substrate particles, the density of the composite coated particles is increased or decreased. The effect of the densities of the particles and of the coat will appear from the following. If \( x \) be the weight percent of the substrate particles in the coated particle and \( d_s \) be the density of the substrate and \( d_c \) be the density of the coated particle, then \( d_p [d_s x + d_c (100 - x)] = 100 d_c d_s \).

The accompanying secondary or primary abrasive particle may or may not be coated and may be chosen to match the particle size of the accompanying particle. We prefer, in order to obtain additional advantages to employ as encapsulating metals, those listed in Table 2. The values are obtained from available literature.

The encapsulation of the abrasive particles with a metallic envelope according to our invention has values in addition to permitting of a uniform distribution of the particles as described above. Where metal is used as a matrix to bind the abrasive particles in the abrader structure, encapsulation of the abrasive increases the grip of the metal matrix on the abrasive particle. Where the bond is weak, the particles are torn out of the metal matrix, causing excessive wear.

The intermetallic bond between the metal matrix and the primary or secondary abrasive increases the retention of the abrasive particle until its cutting life is ended by wearing away of the particle or breaking away of fragments thereof from the portion of the abrasive particle which has become free of the encapsulation at the abrading surface during the abrading action.

In selecting the metal for the envelope when the encapsulated particle is to be used with metal matrix acting as a bonding agent, it is desirable that the metal in the envelope have a suitably higher melting point than the metal matrix. A further advantage of the encapsulated abrasive particle of our invention when used together with a metal matrix resides in the increased rate of heat trans-

### TABLE 2

<table>
<thead>
<tr>
<th>Metal</th>
<th>Specific Gravity</th>
<th>Melting Point °C</th>
<th>Percent Thermal Coefficient of Linear Expansion ( \times 10^6/°F ) 0–1000°F</th>
<th>Young’s Modulus ( \times 10^9 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tungsten (W)</td>
<td>19.3</td>
<td>3380</td>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td>Tantalum (Ta)</td>
<td>16.6</td>
<td>2966</td>
<td>4</td>
<td>27</td>
</tr>
<tr>
<td>Molybdenum (Mo)</td>
<td>10.2</td>
<td>2610</td>
<td>2.2</td>
<td>50</td>
</tr>
<tr>
<td>Niobium (Nb) i.e. Columbium (Cb)</td>
<td>8.5</td>
<td>2500</td>
<td>4</td>
<td>26</td>
</tr>
<tr>
<td>Vanadium (V)</td>
<td>5.89</td>
<td>1890</td>
<td>3.2</td>
<td>41</td>
</tr>
<tr>
<td>Zirconium (Zr)</td>
<td>6.4</td>
<td>1852</td>
<td>3</td>
<td>11</td>
</tr>
<tr>
<td>Titanium (Ti)</td>
<td>4.54</td>
<td>1675</td>
<td>4.7</td>
<td>16.8</td>
</tr>
<tr>
<td>Iron (Fe)</td>
<td>7.86</td>
<td>1535</td>
<td>5.5</td>
<td>28.5</td>
</tr>
<tr>
<td>Cobalt (Co)</td>
<td>8.9</td>
<td>1492</td>
<td>6.85</td>
<td>30</td>
</tr>
<tr>
<td>Nickel (Ni)</td>
<td>8.9</td>
<td>1453</td>
<td>7.2</td>
<td>30</td>
</tr>
<tr>
<td>Copper (Cu)</td>
<td>8.9</td>
<td>1083</td>
<td>9.22</td>
<td>16</td>
</tr>
</tbody>
</table>
from the abrasive particle resulting from the more intimate contact surface between the envelope and the substrate and the envelope and the metal matrix. Heat generated at the abrading surfaces, if not readily transmitted to and absorbed in the metal matrix, acting as a heat sink, will cause a local rise in temperature which may have a deleterious effect upon the life of the abrasive particle.

In order to obtain the adjusted apparent density as well as the increased bond between the abrasive particles and the metal matrix, any convenient method for deposit of the metal envelope on the particle substrate may be employed. Thus electrochemical or electrolytic methods which have been previously employed in coating abrasive particles for use in abrader structure with organic resin will permit of some adjustment of the apparent density of the coated particle. They will also, when used together with a metal bonding agent in our novel abrader structure, result in an improved bond between the metal matrix and the coated particle, due to the improved wetting by the molten metal.

The use of the coated particle in a composite structure employing a metal matrix is an improvement over the use of an abrasive particle coated by an electrochemical or electrolytic process where used with a resin binder. It is similarly an improvement over the use of uncoated abrasive particles with resin or metal binders acting as a matrix for the abrasive particles.

Abrasive particles coated by procedures such as electrochemical and electrolytic processes may result in deposits which are contaminated by intergranular inclusions of impurities from their aqueous environment. Furthermore, the deposits particularly in the case of electrolytic deposits have intergranular planes of weakness and the coating has a relatively low tensile and bending strength. They thus do not improve in any substantial degree the physical properties of the coated particle as compared with the uncoated particle.

We prefer that the metal envelopes which constitute the abrasive particles of our invention employed in the novel abrader structure of our invention differ from the foregoing coatings in composition and crystalline nature.

We prefer to form the metal envelope by a process in which the abrasive particle is coated by means which deposit metal on the abrasive of materials which is substantially free of intergranular impurities.

The deposits according to our preferred procedure constitute a pure metal envelope substantially free of intergranular inclusions.

The preferred metallic envelope is formed of allotrimorphic crystal dendrite grains which start at and extend from the substrate surface in statistical orientation generally perpendicular to local substrate surface, creating a superposition of grain growth interrupted by other grain skeleton deposit on top thereof. The grains thus deposited to form a mechanically interlocked grain structure give to the metal sheath high tensile strength.

We prefer to produce the aforesaid encapsulated abrasive of our invention by a process of chemical vapor deposition, by subjecting the abrasive particles to contact with a volatile metal compound at an elevated temperature sufficient to maintain the metal compound in vapor form and contact the vapor with a solid substrate under metal deposition conditions.

We have also found it useful, where the chemical nature of the abrasive particle substrate permits, to choose metallic envelopes which form a surface chemical bond with the substrate by reason of a limited chemical reaction between the metal and the substrate surface, thus producing an encapsulated particle in the form of a cermet.

The formation of the intersurface bond between the envelope and the substrate is facilitated by the elevated temperature employed in our preferred method of metal deposition.

Where the metal envelope has a coefficient of thermal expansion substantially greater than that of the abrasive particle, by depositing the metal envelope on the substrate particle, at a high temperature, the resultant particle on cooling is placed under compression by the metallic envelope. Thus, the tensile force necessary to rupture the abrasive particle must then be greater than in the case of the unencapsulated particle.

This property has an advantage irrespective of the bonding agent employed and may advantageously be used whether resin or metal acts as the bonding agent.

In order to obtain a compressive force on the substrate, we select a metal for the envelope having a substantially greater coefficient of expansion than the substrate. In such case, when the metal is deposited on the substrate at an elevated deposition temperature, on cooling, the metal sheath will contract more than the substrate, putting the substrate under compression. Since the linear coefficient of thermal expansion of suitable abrasives are in the range of about 1 to about 5 × 10⁻⁵ inches per inch per degree Fahrenheit, we select metal sheaths having a higher coefficient of expansion than the substrate. For example, we select metals having linear coefficients of expansion of about 2 × 10⁻⁵ to about 10⁻⁵ inches per inch per degree Fahrenheit. By matching the coefficients of expansion, as described above, a useful encapsulation may be obtained.

It is useful to remember that the coefficient of cubic expansion may, for the above purposes, be taken as about three times the linear coefficient of expansion. In such a combination the disruptive force sufficient to fragment the substrate particle must be greater than that which would fracture the unencapsulated particle, since it must overcome initially the compressive force which places the underlying substrate in compression.

Thus, for example, if diamond be the substrate, we may use for the purpose any one of the metals listed in Table 2 to form the encapsulating envelope and thereby also increase the apparent density. In each of these cases, the coefficient of linear expansion of the metal is substantially greater than that of diamond, and their use would have the advantage of adding a compressive force upon the diamonds to help in overcoming the tensile forces which would tend to fracture the diamond when used in an abrader structure as the abrasive particle.

In selecting the encapsulating metal with the view of obtaining the advantage of the differential contraction, metals may be selected, depending on the stress desired to be imparted, for example, for the metals listed in Table 2 and the abrasives of Table 1, metals having a coefficient greater than the substrate coefficient by
about 5 to 10 percent or more of the value of the coefficient of the substrate. That is, the coefficient of the metal should be about 1.05 or more, for example, up to about seven times the coefficient of the substrate.

In selecting the metal encapsulating material, when employing diamonds as a substrate, when we employ carbide-forming metals, we prefer to employ those which have only a limited reaction rate at the temperatures of deposition, as hereinafter described. For example, we may use molybdenum, tungsten, tantalum, niobium (columbium) and molybdenum, and, among the primary abrasive particles, we prefer to employ diamonds, either the natural or synthetic forms, and prefer to employ tungsten as the encapsulating material, deposited under conditions to produce pure tungsten of the crystal form as described herein.

Where we employ the metal encapsulated abrasive in abrader structures formed by metal bonding the encapsulated abrasive in a metal continuous phase matrix, we prefer to employ as a bonding agent a metal having a significantly lower melting point than the metal sheet of the abrasive substrate. When employing diamonds as the encapsulated abrasive particles, we prefer to limit the melting point of the metal matrix to a temperature below about 2,800°F in order not to expose the diamonds to excessive temperature which may impair the mechanical strength of the diamonds.

Another important consideration is the coefficient of thermal expansion of the metal matrix used as bonding agent. Since, in general, the low melting metals and materials have a high thermal expansion, in the absence of an encapsulating metal which is wetted by the molten metal, the mass of matrix on cooling would tend to pull away from the abrasive material, thus impairing the bond. It is one advantage of the encapsulating metal that the thermal expansion of the metal sheet matches more closely the thermal expansion of the metal matrix and that the interfacial tensions will tend to prevent the pulling away of the metal matrix from the metal sheet. Such metals having melting points so as to be fluid in the formation of the abrader structure, for example, at temperatures below about 2,800°F when employing diamonds are suitable.

However, we prefer to employ such metals which also have the preferred properties as hereinafter described. The metal chosen should be fluid at the temperature at which it is desired to employ the molten metal in forming the composite abrader structure and desirably should have, when solid, ductility as measured in the terms of micro-hardness of below about 400 kg/mm². Desirably, also, it should have a compressive strength above about 150,000 p.s.i., a transverse rupture strength above about 90,000 p.s.i. and an impact strength above about 5 foot pounds.

For this purpose we may use copper-based alloys such as brass and bronze alloys and copper-based alloys containing various amounts of nickel, cobalt, tin, zinc, manganese, iron and silver. Since when using encapsulated diamonds the diamond is protected from attack by the metal, we may use cobalt-based, nickel-based, and iron-based alloys of suitable properties. These alloys are excluded from use as metal matrices when using unencapsulated diamonds because under molten conditions they attack the diamond excessively. Thus we may with the encapsulated diamond, for example, employ the nickel-copper-aluminum-silicon alloy having a melting point below 2,000°F; cast iron, cobalt, chromium, and tungsten alloys having melting points below about 2,800°F may be used.

Where the abrasive particle is a tungsten carbide or diamond particle which is attacked by nickel, cobalt or iron-based alloys, the encapsulation of the tungsten carbide or diamond by a metal envelope of substantially higher melting point according to our invention will prevent the attack which the unencapsulated particle would otherwise suffer under the conditions of fabrication of the abrader structure.

The procedure we prefer because it produces the superior envelope when applied to produce our novel encapsulated abrasive particle is the conversion of a volatile compound of the metal into the metal deposited on the substrate and a gaseous or vaporous reaction product which may be removed from contact with the encapsulated metal. This leaves an envelope substantially free of included impurities.

For this purpose we prefer to use the halides or the carbylons of the metals. Preferably for convenience of operation, we prefer to employ those compounds having a boiling point at atmospheric pressure below the reaction temperature.

While compounds which may be placed in the liquid state and which may be distilled by vacuum distillation or by reduction of their partial pressure by means of a carrier gas are possible, the compounds listed in Table 3, having reasonable boiling points, so that their volatilization may be conveniently allowed are preferred by us.

| TABLE 3 |

<table>
<thead>
<tr>
<th>Table 3</th>
<th>B.P. °C at 760 m.m. *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Carbonyl [Fe(CO)₅]</td>
<td>102.8 +</td>
</tr>
<tr>
<td>Molybdenum Pentachloride [MoCl₅]</td>
<td>268</td>
</tr>
<tr>
<td>Molybdenum Hexafluoride [MoF₆]</td>
<td>35</td>
</tr>
<tr>
<td>Molybdenum Carbonyl [Mo(CO)₅]</td>
<td>154.4</td>
</tr>
<tr>
<td>Tungsten Pentabromide [WBr₅]</td>
<td>333</td>
</tr>
<tr>
<td>Tungsten Hexabromide [WBr₆]</td>
<td>17.5</td>
</tr>
<tr>
<td>Tungsten Pentachloride [WCl₅]</td>
<td>275.6</td>
</tr>
<tr>
<td>Tungsten Hexachloride [WCl₆]</td>
<td>346.7</td>
</tr>
<tr>
<td>Tungsten Carbonyl [W(CO)₅]</td>
<td>175 at 766 m.m.</td>
</tr>
<tr>
<td>Tantalum Pentachloride [TaCl₅]</td>
<td>243</td>
</tr>
<tr>
<td>Tantalum Pentachloride [TaF₅]</td>
<td>229.5</td>
</tr>
<tr>
<td>Titanium Tetrafluoride [TiF₄]</td>
<td>230</td>
</tr>
<tr>
<td>Titanium Hexafluoride [TiF₆]</td>
<td>35.5</td>
</tr>
<tr>
<td>Titanium Tetrachloride [TiCl₄]</td>
<td>136.4</td>
</tr>
<tr>
<td>Columbium Pentabromide [CbBr₅]</td>
<td>361.6</td>
</tr>
<tr>
<td>Columbium Pentachloride [CbCl₅]</td>
<td>236</td>
</tr>
<tr>
<td>Columbium Tetrachloride [CbCl₄]</td>
<td>236</td>
</tr>
<tr>
<td>Nickel Hexafluoride [NiF₆]</td>
<td>4 at 25 m.m.</td>
</tr>
<tr>
<td>Vanadium Tetrachloride [VCl₄]</td>
<td>148 +</td>
</tr>
<tr>
<td>Vanadium Pentachloride [V₂Cl₅]</td>
<td>111 +</td>
</tr>
</tbody>
</table>

* Unless otherwise indicated
our invention a coating of exceptional high strength. It is readily wetted by the molten metal matrixes described above and forms a strong metallurgical bond with the metal matrixes employed in our invention. It is particularly useful where the substrate is diamond or other substrates which will react with the tungsten such as those which form cermets with tungsten.

Our preferred primary abrasive is diamond. Where encapsulated with a metal under the preferred conditions as described herein, it will produce a superior abrader structure of longer life. Where encapsulated with tungsten or other suitable metals as described above, it will after the exposed metal sheet in contact with the work has been worn away be exposed to the work but will otherwise be gripped by the encapsulating envelope which is in turn gripped by the metal matrix.

In place of or in addition to the encapsulated diamond, we may use the other abrasives as described above, preferring among them encapsulated alumina but may also use the other abrasives described above, particularly encapsulated tungsten carbide or silicon carbide as is more fully described below.

The invention will be further described by reference to the following figures:

FIG. 1 is a diagrammatic flow sheet of our preferred process of encapsulation. FIG. 2 is a section through a mold for use in the infiltrant technique of forming abrasives according to one form of our invention.

FIG. 5 is a sectional view taken on 5—5 of FIG. 2.

FIG. 3 is a schematic showing of a mold for use in a hot press technique employed in forming an abrader element.

FIG. 4 is a sectional view taken on line 4—4 of FIG. 3.

FIG. 6 shows one application of a shaped abrader according to our invention to a saw.

FIGS. 7—12 are photomicrographs of an etched section of a coated abrasive particle contained in a metal matrix according to our invention.

FIG. 1 illustrated a flow sheet of our preferred process for producing the novel encapsulated abrasive of our invention. The particles to be coated are placed in the reactor 1, whose cap 2 has been removed. The reactor has a perforated bottom to support the particles of selected mesh size. With cap 2 replaced and the valves 3, 4, 5, and 13 closed, and with valve 7 open, the vacuum pump is started to de-aerate the system. Valve 7 is closed and the system is back filled with hydrogen from hydrogen storage 11, valve 5 being open.

The reactor is heated by the furnace 9 to the reaction temperature, for example, from about 1,000°F. to about 1,200°F., while purging slowly with hydrogen. The hydrogen flow rate is increased until a fluidized bed is established. Hydrogen prior to introduction into the reactor passes through a conventional palladium catalyst to remove any impurities, such as oxygen in the hydrogen. Vaporized metallic compound is discharged from the vaporizing chamber 10, which may if necessary be heated by furnace 14, together with an inert gas, for example, argon from argon storage 6 into the reaction chamber.

Preferably we desire to employ the volatile metal halides referred to above, although, in some cases, we may use the carbonyls listed in Table 3. Where the halide is employed, the reaction forms hydrogen halide, which is passed through the bubble traps and is absorbed in the absorber. Where the volatile compound employed is a fluoride, the product formed is a hydrogen fluoride, and we may use sodium fluoride for that absorption. We prefer to employ hydrogen in stoichiometric excess.

The reaction deposits metal on the substrate and the effluent material, being in the vapor state is discharged, leaving no contaminants on or in the metal. The metal is formed in its pure state. The rate of metal deposition depends on the temperature, and flow rate of the reactants, being the greater the higher the temperature and the greater the flow rate of the hydrogen and volatile metal compound.

After the deposit is formed, the valves 4 and 5 are closed and argon is continued to pass into the reactor and the metal encapsulated abrasive is allowed to cool to room temperature in the non-oxidizing condition of the argon environment.

The conditions in the reactor, both because of the mesh size and particle size distribution of the particles and because of the velocity of the vapors and gases fluidizes the particles. As will be recognized by those skilled in the art, a dense phase is established in the lower part of the reactor in which the particles are more or less uniformly distributed in violent agitation in the dense phase. This results in a substantially uniform deposit per unit of surface of the particles.

The reaction products and the carrier gases and excess hydrogen enter the upper space termed the disengaging space where they are separated from any entrained particles.

Where the diamond particle is smooth as, for example, in the case of synthetic diamonds, we may improve the bond of the metal envelope to the substrate diamond surface produced in the process described above by first surface etching of the diamond. The etching of the diamonds will also have an advantage where the metal envelope is produced by other processes such as electrochemical or electrolytic deposition methods. However, for the reasons previously described, the product produced by the process of vapor deposition described above is superior and is preferred by us.

EXAMPLE 1

To etch the diamonds, we immerse them in a molten bath of an alkali metal nitrate or alkaline earth nitrate at a temperature below the decomposition temperature; thus in using potassium nitrate, temperature would range from 630°F. and under 750°F.; sodium nitrate, about 580°F. and under about 700°F.; barium nitrate, at or above 1,100°F. and below its decomposition temperature. We prefer to employ potassium nitrate at about 630°F. for about an hour. The bath is contained in a nitrogen or other inert gas atmosphere.

At the completion of the heating process, the molten bath is cooled and the cooled bath is then leached with water to dissolve the salt, leaving the etched diamonds which may then be separated and dried.

The degree of etching depends upon the immersion time and a suitable time will be about an hour under which conditions the particles will lose from about 1/2 to 2 percent of their weight. The surface of the diamonds is roughened and pitted and forms a desirable and improved substrate base.

For purposes of illustration, not as limitations of our invention, the following examples are illustrative of the
process of depositing a metal sheath upon a substrate.

EXAMPLE 2

Diamonds, either synthetic or natural, preferably etched as above, of mesh size suitable for fluidizing are introduced into the reactor 1. The actual mesh size employed depends upon the service to which the abrader is to be placed. For use in oil well tools, cutters, saws, and grinders, we may use particles of size (Tyler mesh) through a 16 and a 400 mesh (~16 + 400). Preferably we employ 50 to 100 mesh material, for example, 40 + 50 mesh. In depositing tungsten, we may and prefer to employ tungsten hexafluoride, which is contained and vaporized in 10. It is volatile at atmospheric temperatures and need not be heated. In the reactor employed after the system has been de-aerated and back filled, hydrogen flow is established at a low flow rate of about 100 ml/min and as described above, the temperatures in the reactor 1 having been adjusted to 1,150°F., as measured by the thermocouples, the hydrogen flow is increased to about 1,200–1,350 ml/min, and the flow of the tungsten hexafluoride vapor to about 150 ml/min and the argon gas is adjusted to about 285 ml/min, all as measured by the flow meters as indicated in FIG. 1, the hydrogen being in stoichiometric excess over the tungsten hexafluoride.

The thickness of the coat of the tungsten on the diamond depends on the duration of the treatment and suitably for the 40 to 50 mesh diamonds described above, the coat will be 1 mil thick in about 1 hour. Suitable thickness deposit will run from about 0.1 to about 1 mil thick.

The thickness of the coat will also determine the apparent density \(d_p\) of the particle as described above.

It will be seen that with the apparent density of the coated particle for a diamond of 3.5 specific gravity and tungsten of 19.3 specific gravity we may obtain a tungsten coated diamond particle of apparent density \(d_p\) above 3.5 and below 19.3 depending on the weight percent of the tungsten deposited. As stated above, this may vary from an apparent density of 4 to an apparent density of 17 by depositing tungsten from about 14.65 percent of the weight of the coated particle for an apparent density of 4 to tungsten of a weight percent of 96.9 percent of the coated particle for an apparent density of 17. For other densities, the formula given above will indicate the weight percent of the coating metal required to adjust the apparent density of the diamonds to the desired amount by regulating the rate of reaction by adjusting the temperature and the concentration of the reactants and duration of treatment such desired deposits of encapsulating metal may be achieved.

EXAMPLE 3

Instead of diamonds, we may use alumina. The mesh size, temperature, and procedure as described in Example 1 may be followed to produce a tungsten coat of the weight percent described. Since the alumina and diamonds are of analogous density, what has been stated with regard to the required weight percent (in the case of diamonds) of the encapsulating metal applies here as well.

EXAMPLE 4

Similarly, a tungsten carbide may be coated with tantalum to adjust the weight percent as has been described above, following the procedure described in Example 1.

EXAMPLE 5

The process of Example 2 was employed in coating silicon carbide particles of ~80 + 100 mesh. The density of silicon carbide approximates that of diamonds; what has been said of the required percent of tungsten carbide to adjust the apparent density of the coated diamonds applies as well to the silicon carbide.

In the above examples, the substrate surface is completely coated, indicating that the process of vacuum chemical vapor deposition has great Thriving power. The outer surface of the coated particles is topographically congruent to the outer surface of the underlying substrate and reproduces it. The interlocked structure produces a coating of high tensile and bending strength. Since the coating is produced at high temperature, on cooling the contraction of some 1,100°F. will be substantially in excess of the contraction of the substrate as described and the resultant eventual contraction will produce a compressive of the underlying abrasive particle.

The metal coated particles may be employed in producing improved abrader structures from mixtures of primary and secondary abrasives by techniques previously used with such mixtures employing unencapsulated abrasive particles. These include what have become known as infiltration, hot pressing, and flame metallizing procedures.

In producing such abrader structures, we prefer for reasons previously described to adjust the apparent densities of the primary and secondary abrasive particles.

Where the abrader is made up of a single type of abrasive particle, for example, any of the suitable particles of Table I selected as described above and having a specific gravity less than the metal used as a matrix where the abrader is to be formed from a mixture of the abrasive and metal powder, we may wish to adjust the specific gravity of the abrasive to bring it more closely to the metal.

By encapsulating the abrasive of specific gravity different from the metal matrix with a metallic envelope of different specific gravity, we may adjust the apparent density of the encapsulated abrasive to approximate that of the metal matrix.

We can similarly by selecting the substrate and the coating metal and the weight percent of the coat which is deposited obtain an abrasive particle of desired apparent density and match the densities of the primary and secondary particles and the binder metal. For example, by adjusting the weight percent of the tungsten on the above diamonds to about 61 percent, we can obtain a particle of about 7 grams/cc density and by coating tungsten carbide with titanium to 54 percent by weight of the coated particle, we can obtain a particle about 7 grams/cc density, which will approach the specific gravity of suitable binder metal.

It may not always be necessary to equalize the apparent densities of the primary and secondary particles or also that of the binder metal, if desired, for merely by approaching each other by encapsulation of one or the other of the particles according to the principles previously described, an improved distribution of each of the particles may be obtained. For purposes of produc-
ing a uniform mixture of primary and secondary abrasive particles, the apparent densities of the particles of primary and secondary abrasives may be adjusted so that the difference in the apparent densities after adjustment according to our invention shall be equal to about 40 percent to 80 percent or less of the difference in the specific gravity of the unencapsulated abrasives. More preferably we may reduce the difference between the particles to under about 25 percent. Desirably we may produce particles of primary or secondary abrasives of lowest apparent density of about 30 percent or more and preferably 80 to 100 percent of the density of the particle of highest density by encapsulating one or the other or both of the primary and secondary abrasive particles.

Thus, for example, a coat of tungsten metal (19.3 sp. g.) of about 98.7 percent by weight of a coated diamond particle 3.5 sp. g. will match the specific gravity of a eutectic carbide of 15 specific gravity.

By coating the tungsten carbide with titanium sp.g. 4.54, we may reduce the apparent density of the tungsten carbide and thus require a lesser coat on the diamond particle to match.

By coating the tungsten carbide used, molybdenum or any of the other metals listed in Table 2 having lower specific gravities reduce the apparent density of the coated particle.

Where the primary abrasive is diamond and the secondary abrasive is tungsten carbide, we may use any of the metals listed in Table 2 to increase the apparent density of the diamond particle to bring it more closely to the density of the particle of the secondary abrasive and the binder metal if, for example, the hot press method is employed.

We prefer where the continuous phase of the matrix is metallic, in order to obtain additional advantages, to employ as encapsulating metals, those listed in Table 2. The values are obtained from available literature.

The encapsulation of the abrasive particles with a metallic envelope according to our invention has values in addition to permitting of a uniform distribution of the particles as described above.

The secondary abrasive used in the above construction may be usefully a tungsten carbide ranging from WC having 6.12 weight percent of carbon to W.C having a carbon content about 3.16 weight percent. A useful material is so-called sintered tungsten carbide and consists of microsized WC crystals and cobalt metal bonded by liquid phase sintering at high temperature. The cobalt content varies from 3 weight percent to over 25 weight percent. This material has a hardness of about 1250 to 1350 kg/mm² (Knoop). Another form of eutectic alloy containing about 4 percent by weight of cobalt having a hardness in the range of 1,900 to 2,000 kg/mm² (Knoop) may also be used.

EXAMPLE 6

FIGS. 2 and 5 show a suitable graphite mold for use with the infiltrant technique for producing saw blade segments to be brazed to a saw blade. The mold is composed of a base 101, the mold proper 102, with an anchor 103, carrying a funnel 104, clamped by clamp bolt 105, and covered with a furnace cap 106. The mold proper consists of circumferentially space mold cavities having substantially smaller circumferential extension than their radial length. The primary abrasive, for example, a mix of tungsten encapsulated diamond particles -20 + 45 or -45 + 60 screen having a density of about 7 and titanium encapsulated powdered tungsten carbide with a density of about 7 is tamped into the mold 102. The funnel contains a bronze-copper-tin alloy powder through a 200 mesh screen. The diamonds form about 25 percent by volume of the mixture of metal and diamond finally formed in the mold cavity 103. The mold is heated to about 2,000°-2,100° F, to melt the alloy which percolates through the interstices between the diamond particles in the mold cavity, i.e., infiltrates the pores filling them to form the continuous phase binding the coated diamond particles and the tungsten carbide in the continuous metal matrix.

Tungsten carbide may be coated, for example, with molybdenum, tungsten, titanium or niobium. Preferably, however, we prefer to employ molybdenum or titanium or columbium and to encapsulate the secondary abrasive by the process previously described.

The coated tungsten carbide may be replaced by coated secondary abrasive as described above, for example, tungsten coated alumina or silicon carbide. The metal envelope may be tungsten or any other metal chosen as described above.

Instead of employing the infiltrant process, we may employ a hot press procedure to formulate the abrader of our invention. In such procedure, the mixture in the mold is a mixture of abrasive particles and powdered metal which is to form the continuous metal matrix to bond the abrasive particles.

EXAMPLE 7

The mold employed is shown in FIGS. 3 and 4. The mold is similar to that of FIG. 2 except that no funnel is employed and the nut 105 is now a plug 107 and the funnel 104 is replaced by the cap 108 in place of cap 106. The mold is formed for the insertion of the cap as shown. The secondary abrasive may be coated abrasive as described in connection with Example 6.

To produce the saw blade element (See FIG. 6) according to the hot press method described above, an intimate mixture of titanium encapsulated tungsten carbide and tungsten coated diamond of -35 + 50 mesh which has been coated with a tungsten metal envelope to a density of about 7 to match the density of the encapsulated tungsten carbide as described above and a -200 mesh bronze-tin alloy are tamped into the mold of FIGS. 4 and 5. The concentration of diamonds in the mix may suitably be the same as described in connection with Example 7. The mold is heated to about 1,600°F at about 3,000 p.s.i. pressure to produce a saw blade element as described above.

For example, employing the procedures of Examples 7 and 8 in forming a 12-inch saw blade on which about 19 of the above sections are brazed at the periphery of the saw blade, sections of about 3-7/8 inches long, one-eighth inch wide, and about five thirty-seconds inch thick may be formed suitably by introducing about 3,500 stones of mesh size -45 + 60 grit or about 1.1 carats of diamond grit. The abrader will be in the form suitable to be mounted by brazing to a saw blade as shown in FIG. 6.

Instead of metal coated tungsten carbide, we may use another metal coated secondary abrasive described above, for example, metal coated alumina or silicon carbide as described above.
Instead of using the low temperature melting bronze as in Examples 6 and 7, we may use the higher melting metals as binder matrix such as iron, cobalt, nickel or alloys of these metals and heat the hot press mold to temperatures as high as above 1,535°F. depending on the melting point of the metal selected to form the binder.

In producing the encapsulated abrasives employed in the processes of Examples 7 and 8, we prefer to employ the process of encapsulation described in Example 2 and where diamonds are referred to we prefer, where they are synthetic diamonds having a smooth face, that this be etched, for example, by the procedure of Example 1.

The superior product produced by the encapsulation method of Examples 1 and 2 when used in the production of the abraders by the hot press or infiltrant method is illustrated in

FIG. 7 which shows a 0.025 inch tungsten coat on an alumina particle in the metal matrix at 140 X magnification.

FIG. 8 shows a similar tungsten coated alumina particle in a metal matrix at 280 X magnification.

FIG. 9 shows a 0.05 micron tungsten coated diamond particle hot pressed into a metal matrix at 210 X magnification and FIG. 10 shows a portion of the particle at 840 X magnification.

FIG. 11 shows 80-100 mesh silicon carbide particle coated with tungsten, hot pressed into a metal matrix at 280 X magnification.

FIG. 12 shows tungsten coated Al₂O₃ hot pressed in a metal matrix at 1,700° polished and etched to show the allotriomorphic dendrite crystals.

It will be seen the excellent throwing power of the process and the intimate coating produced. The metal sheath is congruent to the substrate surface coproducing it faithfully. The resultant intimate bond produces the advantages of compression and hot transfer as referred to above.

The crystal forms will be seen to be allotriomorphic with the interlocked dendrites as described above.

We claim:

1. A shaped abrader comprising a continuous phase of a metal matrix, primary abrasive particles and secondary abrasive particles, said primary and secondary abrasive particles being of different densities, the primary abrasive particles having a hardness more than 2,000 kg/mm², and said secondary abrasive particles having a hardness of about 1,250 kg/mm² and less than the hardness of the primary abrasive particles, the particles of lower density, being encapsulated in a metal envelope, the densities of said encapsulated particles of lower density being greater than the density of the unencapsulated particles of lower density, said encapsulated particles having a density more than 30 percent of the density of highest density, and said particles being substantially uniformly distributed in said metal matrix.

2. The abrader of claim 1 in which said primary abrasive is diamond and said secondary abrasive is an inorganic compound having a hardness of at least about 1,250 kg/mm².

3. The abrader of claim 1 in which the encapsulating metal is chosen from the group consisting of tungsten, tantalum, columbium, molybdenum and titanium.

4. In the abrader of claim 1 in which the secondary abrasive is metal encapsulated with a member of the group consisting of tungsten carbide and alumina and silicon carbide.

5. In the abrader of claim 4 in which the primary abrasive is metal encapsulated diamonds and the secondary abrasive is a member of the group consisting of metal encapsulated tungsten carbide, metal encapsulated alumina and metal encapsulated silicon carbide.

6. In the abrader of claim 1 in which the primary abrasive is diamond encapsulated with a metal and the secondary abrasive is alumina encapsulated with a metal.

7. The abrader of claim 1 in which the primary abrasive is diamond encapsulated with tungsten and the secondary abrasive is tungsten carbide.

8. The abrader of claim 1 in which the primary abrasive is diamond encapsulated with tungsten and the secondary abrasive is alumina encapsulated with tungsten.

9. The abrader of claim 1 in which the primary abrasive is diamond encapsulated with tungsten and the secondary abrasive is silicon carbide encapsulated with tungsten.

10. The abrader of claim 1 in which the primary abrasive is diamond encapsulated with tungsten and the secondary abrasive is tungsten carbide encapsulated with a metal having a specific gravity less than the specific gravity of the tungsten carbide.

11. The abrader of claim 10 in which the metal encapsulating the tungsten carbide is a metal having a specific gravity less than 15.

12. The abrader of claim 11 in which the metal encapsulating said tungsten carbide is chosen from the group consisting of molybdenum, columbium, and titanium.

13. In a hot press process for producing a shaped abrasive in which an intimate mixture of primary and secondary abrasive particles and a powdered metal is positioned in a mold which is heated and subjected to elevated pressure on said mixture, the improvement in which said particles are composed of a primary abrasive having a hardness of about 2,000 kg/mm², and said secondary abrasive particle having a hardness in excess of about 1,250 kg/mm², and less than the hardness of the primary abrasive particles, the primary abrasive particles having a different specific gravity from the specific gravity of the secondary abrasive particles, the primary or the secondary abrasive particles being encapsulated in a metal envelope, the densities of the encapsulated particles of lower density being more than 30 percent of the density of the particles of highest density and said particles being substantially uniformly distributed in said metal matrix.

14. In the process of claim 13 in which said primary abrasive is diamond and said secondary abrasive is an inorganic compound having a hardness of at least about 2,000 kg/mm².

15. In the process of claim 13 in which the encapsulating metal is chosen from the group consisting of tungsten, or tantalum, columbium (niobium) molybdenum and titanium.

16. In the process of claim 13 in which the secondary abrasive is chosen from the group consisting of metal encapsulated tungsten carbide metal encapsulated alumina and metal encapsulated silicon carbide.

17. In the process of claim 13 in which the primary abrasive is metal encapsulated diamonds and the sec-
ondary abrasive is chosen from the group consisting of metal encapsulated tungsten carbide, metal encapsulated alumina and metal encapsulated silicon carbide.  

18. In the process of claim 13 in which the primary abrasive is diamond encapsulated with a metal and the secondary abrasive is alumina encapsulated with a metal.

19. In the process of claim 13 in which the primary abrasive is diamond encapsulated with tungsten and the secondary abrasive is tungsten carbide.

20. In the process of claim 13 in which the primary abrasive is diamond encapsulated with tungsten and the secondary abrasive is silicon carbide encapsulated with tungsten.

21. In the process of claim 13 in which the primary abrasive is diamond encapsulated with tungsten and the secondary abrasive is alumina encapsulated with tungsten.

22. In the process of claim 13 in which the primary abrasive is diamond encapsulated with tungsten and the secondary abrasive is tungsten carbide encapsulated with a metal having a specific gravity less than the specific gravity of the tungsten carbide.

23. In the process of claim 13 in which the metal encapsulating the tungsten carbide is a metal having a specific gravity less than 15.

24. In the process of claim 13 in which the encapsulating metal is chosen from the group consisting of molybdenum, columbium, and titanium.
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,841,852 Dated October 15, 1974

Inventor(s) ARTHUR G. WILDER and HAROLD C. BRIDWELL.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 5, line 52: "trimorphic" should read --triomorphic--.

    line 63: "volatile" should read --volatile--.

Column 6, line 44: "distruptive" should read --disruptive--.

    line 46: "unencapsulated" should read --unencapsulated--.

Column 9, line 9: "encasulated" should read --encapsulated--.

    line 26: start new paragraph beginning with

    "Fig. 2 is----".

Column 11, line 11: after "and" insert --on--.

    line 22: "1,200" should read --1,250--.

Column 12, line 28: "ouslyused" should read --ously used--.

Signed and sealed this 7th day of January 1975.

(SEAL)

Attest:

McGOY M. GIBSON JR. C. MARSHALL DANN
Attesting Officer Commissioner of Patents