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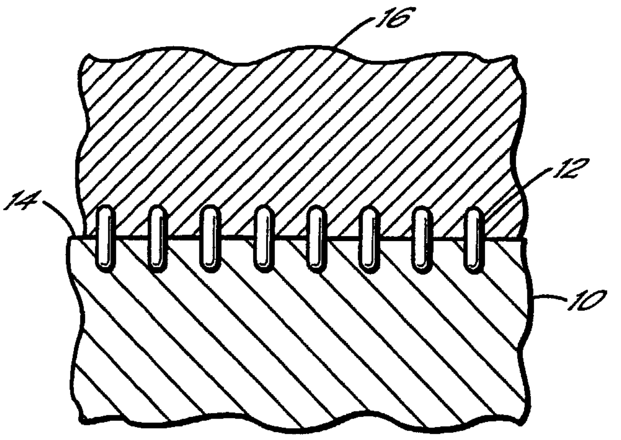
(54) Title: ADHERENT HARD COATINGS FOR DENTAL BURS AND OTHER APPLICATIONS



(57) Abstract: A method is provided for forming strongly adherent hard material coatings on various article substrates (10). A plurality of discrete particles (12) are attached to a substrate surface (14) such that the particles (12) are at least partially embedded in the substrate surface (14) and protrude outwardly relative to the substrate surface (14). The substrate surface (14) having the outwardly protruding particles (12) is thereafter coated with a hard material (16), including generally those materials having a hardness greater than the hardest steel. There is formed thereby an article (10) having a substrate surface (14) coated with a hard material (16) that is strongly adhered to the substrate surface (14) by discrete particles (12) that form a mechanical interlock between the substrate (10) and the hard material coating (16).

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ADHERENT HARD COATINGS FOR DENTAL BURS AND OTHER APPLICATIONS

Field of the Invention

This invention relates to the manufacture of various articles having adherent hard coatings, and more particularly to the application of hard coatings on dental burs.

Background of the Invention

The production of discrete particles or continuous, conformal, polycrystalline diamond films or coatings by CVD (chemical vapor deposition) techniques is a well established technology. It typically involves the breakdown of carbon-containing fluids (gases and/or liquids) in a high energy environment to which superabundant concentrations of hydrogen (and, sometimes, minor amounts of other gases) are added. Carbonaceous radicals and other species released from the fluids condense on top of substrates normally kept in the 700 -

1,000°C temperature range. The hydrogen acts as an etchant in its monoatomic state and essentially removes all non-diamond phases condensed on the substrates. Thus, small diamond nuclei are left on the substrate surface, which grow and interlock into a polycrystalline, continuous film or coating. In this way, many of the outstanding properties of pure diamond can be engineered into a variety of new products coated with CVD diamond layers. Some of these properties, such as the extremely high hardness, wear resistance, chemical inertness, and biocompatibility of diamond, make it an almost ideal coating material for dental burs.

Despite the impressive progress made in this field in recent years, which has seen increasingly sophisticated deposition devices and techniques, for example, as described in U.S. Patent Nos. 5,749,955 and 5,722,046, and correspondingly higher deposition rates (up to about 1 mm/hr), an inherent difficulty in attaining sufficient bonding strength between diamond coatings and substrates has hindered much of the usefulness and commercial applicability of this technology.

From a mechanical standpoint, the problem stems from high interfacial stresses that arise due to thermal contraction mismatches between diamond and most substrate materials as they cool down from the elevated deposition temperature range. Some of the approaches that have been tried to overcome this aspect of the problem include: (a) limiting substrate choices to materials with low thermal expansion coefficients similar to that of diamond, for example, molybdenum, silicon nitride, or cemented carbides of low binder content; (b) employing stress relieving thermal treatments as, for example, in U.S. Patent No. 5,701,578; (c) managing stress/strain levels in the coatings as, for example, in U.S. Patent Nos. 5,633,087 and 5,286,524; and (d) applying intermediate layers of softer materials to accommodate interfacial stresses as, for example, in U.S. Patent No. 5,688,557.

From a chemical standpoint, poor adhesion strength of diamond coatings derive from chemical interactions with substrates that show high affinity for carbon at elevated temperatures. Cobalt and nickel, two of the most widely used binders for cemented carbides, and iron, the base material of steels and other ferrous alloys, are prime examples. These elements can dissolve large amounts of carbon at high temperatures and tend to graphitize the substrate-diamond interface. Some of the reported methods to reduce or eliminate this effect include: (a) removal of Co or Ni from a thin superficial layer in cemented carbide substrates by means of chemical etching as, for example, in U.S. Patent Nos. 5,713,133, 5,700,518, 5,567,526 and 5,236,740, or by means of thermal treatments as, for example, in U.S. Patent Nos. 5,716,170, 5,701,578, 5,068,148, 5,648,119 and 5,585,176, or by means of a combination of chemical etching and thermal treatment as, for example, in U.S. Patent Nos. 5,660,881, 5,618,625, 5,415,674 and 5,204,167; and (b) use of interlayers or chemical barriers as, for example, in U.S. Patent Nos. 4,992,082, 4,988,421, 4,919,974 and 4,734,339.

While the removal of the Co or Ni binder may be effective in improving the diamond adherence to cemented carbides, it is believed that such removal weakens a thin substrate surface layer, which can lead to coating failure. Rather than breaking at the interface, the coating is lost due to mechanical failure of the substrate material a few microns into the Co- or Ni-depleted and weakened carbide layer.

Current trends toward improving the adherence strength of CVD diamond coatings to their underlying substrates are based on a combination of mechanical and chemical effects.

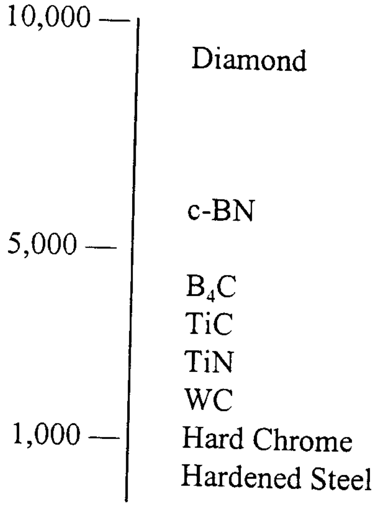
U.S. Patent Nos. 5,716,170, 5,701,578, 5,648,119 and 5,585,176 describe a successful method applicable to cemented carbide substrates. Prior to the CVD diamond coating, the carbide parts are subjected to heat treatments at very high temperatures and under subatmospheric pressure of nitrogen for several hours. Such treatments not only promote a very superficial Co or Ni binder removal but also cause considerable carbide grain growth at the substrate surface. The heat treatment conditions are tailored to obtain a certain minimum surface density of very large and protruding carbide grains which have been found to become effective mechanical anchoring sites for the subsequently grown CVD diamond coating. This method, however, is applicable only to cemented carbide parts and only to those that can withstand the harsh thermal treatment conditions without appreciable dimensional distortions. It is not suited for small, precisely ground articles such as dental burs.

U.S. Patent No. 5,776,355 describes a method of preparing substrate materials for diamond deposition based on a similar principle. Patterns of parallel or cross hatched grooves are scored onto the substrate surface to create the mechanical interlocking effect. This method, however, fails to address the chemical interaction problem.

U.S. Patent No. 5,772,336 discloses strongly adherent CVD diamond coatings obtained on cemented carbide tool surfaces having a plurality of wave-like projections on their surfaces. This method also fails to address the chemical interaction problem.

Other hard coatings, besides diamond, also suffer from adherence problems. Any material harder than the hardest steel is generally classified as a "hard material". The following diagram shows the relative Vickers hardness values of some hard materials:

VICKERS HARDNESS NO.



Except for c-CN, which has been theoretically predicted to be harder than diamond, no other known material matches the hardness and wear resistance of diamond.

When applied by PVD (physical vapor deposition) methods, hard coatings show inherently lower adhesion strengths to substrates than CVD produced films. This is explained by the typically low PVD deposition temperatures which do not allow any appreciable atomic thermal interdiffusion to take place between the coatings and substrates. Hence, PVD coatings are not suitable for high temperature applications (above 500°C) and are generally limited to only about 5μm in thickness.

Although CVD hard coatings are generally more adherent and may be grown to thicker layers, they still suffer from the thermal expansion mismatch problem that hinders most of the usefulness of diamond coatings. The following table presents thermal expansion coefficients at room temperature for some hard materials:

Material	**α x 10^{-6} (°C^{-1})**
Diamond	2-3
Si_3N_4	2.8
SiC	5.4-6.8
WC-Co	5.5-5.9
HfC	6.1-6.6
VC	7.2
TiC	7.4-8.8
α-Al_2O_3	8.3-9.5
TiN	9.4
Cr_2C_3	9.5

Another critical parameter affecting the adherence strength of hard coatings is their ability to yield and deform under external loading and/or interfacial, residual stresses without cracking or peeling off. In general, the harder the material, the less compliant it is. Therefore, well adherent CVD diamond coatings are among the most difficult ones to be obtained.

The bonding strength may also be severely impaired by chemical interactions between hard coatings and substrates. Some of the most important cases occur in the CVD deposition of carbides onto parts that have a large affinity for carbon at high temperatures (e.g., steels, cemented carbides). CVD coatings of TiC, VC, HfC, or diamond applied onto WC-Co or steels usually require some sort of pre-treatment of the substrate surface to avoid undesirable, bulk carburization of the parts before the hard coatings can actually start to form.

There is thus a need to provide a method for firmly attaching CVD diamond coatings and other hard material coatings onto substrates, such as dental burs.

Summary of the Invention

The present invention provides a method for forming strongly adherent hard material coatings on various article substrates. To this end, and in accordance with the principles of the present invention, a plurality of discrete particles are attached to a substrate surface layer such that the particles are partially embedded in the substrate, or in an intermediate layer coated on the substrate, and protrude outwardly relative to the substrate surface layer. The substrate surface layer having the outwardly protruding particles is then coated with a hard material. There is formed thereby an article having a substrate surface coated with a hard material that is strongly adhered to the substrate surface by discrete particles that form a mechanical interlock between the substrate and the hard material coating. The hard material coating is a material having a hardness greater than the hardest steel, such as diamond, diamond-like materials, carbon nitride, cubic boron nitride, titanium nitride, titanium carbonitride, silicon carbide, and other $X_aY_bZ_c$ compounds and/or mixtures/multilayers of uniform/graded compositions where X, Y and Z are elements selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Al, Si, C, N, O or B; and a, b and c are non-negative integer numbers.

These and other objects and advantages of the present invention shall become more apparent from the accompanying drawings and description thereof.

Brief Description of the Drawings

The accompanying drawings, which are incorporated in and constitute a part of this specification, illustrate embodiments of the invention and, together with a general description of the invention given above, and the detailed description given below, serve to explain the principles of the invention.

FIG. 1 is a cross-sectional view of a first embodiment of an article made by the method of the present invention;

FIG. 2 is a cross-sectional view of a second embodiment of an article made by the method of the present invention;

FIG. 3 is a cross-sectional view of a third embodiment of an article made by the method of the present invention; and

FIG. 4 is a cross-sectional view of a fourth embodiment of an article made by the method of the present invention.

Detailed Description

The present invention provides a method for promoting strong adherence between a variety of substrate materials and hard coatings by the use of an intermediate layer of outwardly protruding anchoring particles bonded to, and extending into, the surface layer of the substrate. This method is applicable to a large number of products and articles, and is not limited or restricted to the preferred conditions or examples outlined below in regards to CVD diamond coated dental burs. For example, in addition to dental burs, other applications of the present invention include coatings on dental files, pliers, cutting/abrasive wheels, drills and other dental instruments; on dental implants; on cutters, files, markers, drills, engraving tools and other articles used in the jewelry and glass industries; on medical/surgical knives, scalpels, bone implants and other medical articles; on cutting tools for the metal forming and wood cutting industries, including indexable inserts, drills, taps, reamers, cutting/abrasive wheels/stones, etc.; for wear resistant surfaces in micrometers, callipers, bearings, nozzles and wire transport guides; for chemically inert surfaces used in laboratory hardware and appliances or in lithographic maskings; on extruding dies, wire drawing dies and other metal forming tools; on electronic heat sinks, electronic packaging devices and other electronic/power components; and for radiation resistant surfaces for nuclear instruments, satellite components and other space bound devices.

As used herein, the term "hard" in the context of "hard coatings" is intended to encompass a wide variety of materials including but not limited to diamond. Generally speaking, the "hard" coatings contemplated by the present invention include coatings of materials having a Vickers hardness value greater than the hardness value of the hardest steel, which said steel has a Vickers hardness value on the order of about 1,000.

The first step in the method of the present invention is selecting an appropriate substrate material. The material should be capable of withstanding temperatures used in the coating process, up to about 1100°C for diamond CVD, without degradation of properties. Further, the material should have an average linear thermal expansion coefficient in the 25-1000°C range not greater than $12x10^{-6}°C^{-1}$, and preferably in the range less than $8x10^{-6}°C^{-1}$. For example, cemented carbides, such as straight cemented carbide having 6% or less Co binder (WC-Co≤6%); steel; silicon nitrides; Ti/Al/V alloys, such as Ti/6Al/4V (Ti-grade 5 per ASTM specification); Ti/Al/V/Sn alloys; Fe/Ni/Co alloys, such as KOVAR® (having an approximate composition of Fe/29Ni/17Co (available from Carpenter Alloys, Reading, PA); Mo; Cu; Ti; W; Ta; Va; and low thermal expansion coefficient materials are suitable substrate materials for dental burs and a variety of other applications.

Before coating, the article may need to be manufactured observing all specifications and dimensional tolerances for the particular article, but allowing up to 10-150μm for linear dimensional increase in the region to be coated. The linear dimensional increase needed is dependent on the size of the discrete particles, which vary from about 10μm up to about 250μm.

The second step in the method of the present invention is to firmly attach to the substrate area to be coated a distribution of discrete particles in appropriate sizes and shapes so as to form a densely packed and uniform distribution of protruding anchoring sites on the substrate surface. These particles may be directly embedded into the substrate surface to be coated or they may be attached to it by means of an intermediate binding layer of a suitable material. Thus "substrate surface layer" as used herein includes the surface portion of the substrate itself and intermediate binding layers on the substrate. The surface density of the protruding particles should be in the range of about 2% to about 100% of the total surface area to be coated, and preferably in the range of about 50% to about 85% of the total surface area to be coated. The particles may vary in size from about 10μm up to about 250μm and should be locked into place so that about 10%-90% of their average sizes, advantageously about 50%-75%, are either directly embedded into the substrate surface or into an intermediate binding layer on the substrate. Thus, significant portions of the particles protrude outwardly to provide the desired anchoring sites. Further, particles of any shape may provide adequate mechanical interlocking to achieve strong adherence, but jagged particles are preferred to smooth, round particles.

These particles may be of ceramic and/or metallic materials, comprising one or more phases (for example, single crystals, coated particles, or composites) and may be irregularly (for example, crushed grits) and/or smoothly (for example, spheroids) shaped. Typical materials are natural or synthetic diamond, silicon carbide, silicon nitride, cubic boron nitride, oxides, such as metal oxides and ceramic oxides, reinforced composite materials, such as fiberglass or silicon carbide reinforced metal matrices, and other superhard particles.

Particles of different materials and/or different sizes and shapes may be mixed together to obtain desired properties, such as mechanical toughness and compliance in terms of thermal expansion, and may be attached as a continuous or discontinuous monolayer or as a thick multilayer, as long as the outermost surface to be coated possesses the required distribution of protruding anchoring particles.

Methods of positioning the anchoring particles onto the substrate surface or onto an intermediate binding layer, prior to permanently locking them in place, may involve the use of volatile adhesives such as ethylene glycol, methyl cellulose, hydroxypropyl cellulose, polyethylene, polypropylene and polystyrene. The adhesive is subsequently burned off or vaporized, typically in a vacuum furnace at temperatures below 700 °C. The particles may be randomly positioned onto the substrate surface layer by immersing the article to be coated in a colloidal solution containing the particles and the volatile adhesive or by painting or spraying the volatile adhesive onto the article surface and then blasting the surface with a gaseous jet containing the particles. Alternatively, random positioning of electrically conductive particles on the substrate surface layer may be accomplished by electrophoretic means, in which the particles are "dragged" toward the article by electromagnetic forces. The protruding particles also may be positioned in preferred configurations by magnetic fields and/or by any other suitable aligning method. For example, where surface textures and/or patterns (such as symbols or marks) are desired on the final coated surface, they can be created by selectively positioning the particles by masking the areas not to be coated, such as in lithographic techniques.

Methods of permanent attachment of the particles to the substrate surface layer may include direct surface bombardment or blasting, usually aided by thermal softening of the surface layer, such as by laser-induced surface softening or melting. Alternatively, the substrate surface layer may include an intermediate binding layer into which the anchoring particles are permanently attached. This intermediate binding layer may include a brazing alloy with adequate bonding and wetting properties. The intermediate binding layer may be brazed or plated to the article or may be chemically and/or electrochemically co-deposited together with the particles. Alternatively, the intermediate binding layer may be plasma sprayed onto the part using appropriate mixtures containing the particles and metallic alloys, or the mixture may be deposited by a number of different CVD and/or PVD techniques.

Suitable brazing alloys for permanently securing protruding particles onto a substrate depend on the specific substrate and protruding particle materials being used. In general, Ni/Cr, Ag/Cu and Au alloys may be considered for brazing alloys. By way of example, for a WC substrate with protruding diamond or WC particles, suitable brazing alloys would include Ni/5-26wt.%Cr/<15wt%P,B,Fe; Ag/27wt.%Cu/4.5wt.%Ti; or Au/3wt.%Ni/<1wt.%Ti. For a KOVAR® substrate with protruding diamond or WC particles, a suitable brazing alloy would be Ni/5-26wt.%Cr/<10wt.% Si,B,Fe.

The brazing alloy is typically provided in powder or tape form. The brazing powder is mixed with a volatile binder, as described above, which is then vaporized. In one method, the discrete particles are mixed in with the brazing powder and binder, applied to the substrate, followed by vaporization of the binder. Upon cooling, a hard brazed surface layer is achieved on the substrate, with discrete particles protruding outwardly from the brazed surface layer. Due to the wetting properties of the brazing alloy, some brazing alloys will coat the protruding surfaces of the discrete particles, but a protruding morphology will still be achieved. In another method of brazing, the brazing alloy powder in a binder is applied to the substrate surface, the binder is vaporized, and the brazing alloy is allowed to cool to form a solid surface layer. The discrete particles in a binder are then applied to the substrate surface brazed layer, and the article is heated to both vaporize the binder and melt the brazed layer. Upon melting of the brazed layer, the discrete particles sink into the brazing alloy, thus providing anchoring particles protruding outwardly from the braze coated substrate. To ensure the protruding morphology, the brazed layer or other coating layer should have a thickness of about 5% to about 75% of the average size of the anchoring particles. Finally, particle attachment of the present invention may involve any other method or combination of processes that result in attaining the desired surface distribution of firmly attached protruding anchoring particles.

By way of example, but not intended to limit the scope of the present invention, irregularly shaped particles of natural or synthetic diamond, type A, having an average particle size of 51μm are brazed to a carbide dental bur head surface with a layer of a suitable NiCr brazing alloy having a thickness of about 38μm to produce a closely packed and uniformly dense monolayer of diamond particles firmly embedded in the brazed layer and protruding outwardly an average height of about 25μm.

If necessary, a thin and continuous chemical barrier coating of suitable material(s) may be applied over the entire particle-attached substrate surface. The chemical barrier coating may be about 0.01μm to about 10μm thick, and preferably between about 0.5μm and 5μm. The purpose of the chemical barrier coating is to prevent harmful chemical interactions between the hard coating and the underlying materials. In the case of CVD diamond coatings, appropriate interlayers must create a barrier to C absorption into the particular underlying materials. Further, the barrier material must be capable of withstanding the deposition temperature of the hard coating without deleterious chemical interactions and degradation of properties. Finally, the chemical barrier layer must be compliant, not stiff or brittle, so that the layer does not fracture. Typical materials include boron, titanium boride, titanium nitride, and titanium carbonitride. The chemical barrier layer may be applied by conventional PVD and/or CVD techniques in one or more layers of one or more compounds, as a single, homogeneous structure or as a graded composition barrier. It is important, however, that the discrete particles, now coated, still protrude outwardly from the substrate surface layer to provide the necessary anchoring sites.

Again, by way of example, and not intended to limit the scope of the invention, a stoichiometric TiN coating less than $3\mu m$ thick is applied by a PVD technique over an entire carbide bur head, covering the attached diamond anchoring particles and spaces in between them, but keeping the desired protruding morphology undisturbed.

The third step in the method of the present invention is to coat the prepared surface to achieve the desired and/or required total hard coating thickness. Hard coating thicknesses may range from less than $1\mu m$ to about $300\mu m$, and preferably between about $30\mu m$ and about $150\mu m$. Any available hard coating technique may be employed in the method of the present invention. Such techniques include, by way of example: chemical or electrochemical coating of hard chrome; CVD or plasma enhanced CVD for diamond or diamond-like materials, c-BN, TiN, TiC or TiCN; or cathode arc sputtering, magnetron sputtering, electron beam evaporation, ion plating or plasma spraying for TiN, HfC, VC, TiCN, TiB_2, Cr or WC. For example, adherent diamond coatings may be deposited by CVD onto dental burs. Hard coating materials contemplated by the method of the present invention include those materials having a hardness greater than the hardest steel, which has a Vickers hardness value of about 1,000. Examples include diamond, diamond-like materials (which have some properties similar to those of diamond, but contain various amounts of non-diamond phases), carbon nitride, cubic boron nitride, titanium nitride, titanium carbonitride, silicon carbide, and other $X_aY_bZ_c$ compounds and/or mixtures/multilayers of uniform/graded compositions where X, Y and Z are elements selected from Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Fe, Al, Si, C, N, O or B; and a, b and c are non-negative integer numbers.

Various embodiments of the resulting articles produced according to the method of the present invention are shown in FIGS. 1-4. FIG. 1 shows an article substrate 10 having discrete particles 12 embedded or partially extending into the substrate surface layer 14, with the substrate surface layer 14 and protruding discrete particles 12 coated with a hard coating 16. FIG. 2 shows a chemical barrier coating 18 applied over the substrate surface layer 14 and protruding particles 12 of FIG. 1, with the hard coating 16 applied over the chemical barrier layer 18. FIG. 3 shows a brazing alloy layer 20 applied to the substrate 10, with the discrete particles 12 embedded or partially extending into the surface layer 14 of the brazed layer 20 and the hard coating 16 applied over the brazed layer 20 and protruding particles 12. FIG. 4 shows a chemical barrier layer 18 applied over the brazed layer 20 and protruding particles 12 of FIG. 3, with the hard coating 16 applied over the chemical barrier layer 18.

Examples

Example 1

Dental burs with cylindrical heads were made of cemented carbide with 6% cobalt content. The average linear thermal expansion coefficient of the material is $5.6\times10^{-6}\,^{\circ}C^{-1}$ in the 25-1000°C temperature range. Some of these bur samples, in accordance with the principles of the present invention, had synthetic diamond grit particles in the 230/325 mesh size range (50-70μm average particle size) brazed to the cylindrical heads with a braze material containing 14% Cr, 9% P, balance Ni. Brazing was conducted in a furnace at 950°C for 2 minutes in a dry hydrogen atmosphere. This resulted in closely packed and uniformly dense monolayers of diamond particles firmly attached to the bur heads and protruding an average height of 25-30μm above the braze. Titanium nitride layers of 3-5μm thickness were then PVD deposited onto the brazed bur heads in a chamber filled with a nitrogen gas and titanium vapor mixture at a temperature of about 350-400°C. Other bur samples, for comparative purposes, had no diamond particles attached to the cylindrical head, prior to being PVD coated with titanium nitride to the same final thickness of 3-5μm. The bur samples of the present invention and the comparative bur samples were then placed together in a CVD reactor and coated with diamond at 850°C in a methane-hydrogen gas mixture to produce a 50-60μm thick CVD diamond coating on each sample.

The CVD diamond layers on the comparative bur samples having no brazed anchoring particles cracked and flaked off the bur heads immediately upon cooling down from the 850°C deposition temperature. By contrast, the CVD diamond coatings on the burs of the present invention having the brazed anchoring particles showed no signs of delaminating. The bur samples of the present invention were individually examined under high magnification in a scanning electron microscope (SEM) and weighed to 0.0001g accuracy both before and after being submitted to extensive cutting trials. Each CVD diamond coated bur of the present invention was evaluated in numerous cutting tests performed with a high speed dental turbine cutting through glass and MACOR® bars, which is a ceramic material having hardness and texture similar to that of dental enamel. In all cases, no detectable differences were seen from the visual inspection of the SEM data and from comparison of the weight data collected before and after the cutting tests. Such results demonstrate the excellent adhesion between the CVD hard coatings and substrates prepared according to the principles of the present invention, despite the unusually high thickness of the CVD diamond layers and the high interfacial stresses resulting therefrom.

Example 2

The procedures of Example 1 were repeated with the exception that the 230/325 mesh diamond anchoring particles were nickel plated to the carbide bur heads of the present invention, rather than brazed. The plating also resulted in well-packed and uniformly dense monolayers of diamond particles firmly attached to the bur heads and protruding an average height of 25-30μm. Titanium nitride layers of 3-5μm thickness were then PVD deposited onto the plated bur heads. The CVD diamond coating was deposited at 950°C with the resulting layers having a thickness of 25-35μm. Again, the CVD diamond coatings spontaneously flaked off the comparative bur heads not having the plated anchoring particles, but remained well adhered to the bur heads of the present invention having the nickel plated diamond particles. SEM investigations, weighing, and extensive glass/MACOR® cutting tests as described above were also carried out and again confirmed the excellent bonding strength of the CVD diamond coatings on the bur samples of the present invention.

Example 3

The procedures of Example 2 were followed, with the exception that the 230/325 mesh diamond anchoring particles were replaced by coarse 60/80 mesh diamond particles (208μm average particle size), and the average height of the protruding crystals was 150μm. The CVD diamond coatings were deposited to a thickness of about 50μm. Upon cooling from the deposition temperature of 950°C, only the bur samples of the present invention with the plated anchoring particles retained their CVD diamond coatings. Again, the comparative coatings not having the plated particle layer suffered from cracking and flaking of the diamond coating. The SEM analysis, weight data and glass/MACOR® cutting tests with the dental rotary turbine confirmed the extremely good adherence of the CVD diamond layers for the bur samples of the present invention.

Example 4

Dental burs with cylindrical heads were made of KOVAR®, a metallic alloy containing 17% Co, 29% Ni, balance Fe, with the mean linear coefficient of thermal expansion of KOVAR® being $11.3 \times 10^{-6} °C^{-1}$ in the 25-900°C temperature range. As in Example 2, 230/325 diamond mesh anchoring particles were nickel plated to the KOVAR® bur heads with the same protruding morphology, and titanium nitride was then PVD deposited onto the plated bur heads at a thickness of 3-5μm. CVD diamond coating was performed at 950°C to achieve a deposited layer of 25-35μm thickness. Similar results from SEM, weighing and cutting tests were obtained to that of the previous examples, further demonstrating that CVD diamond coatings adhere very well even to metallic substrates when prepared according to the present invention.

Example 5

Bur samples with a tapered, fine-pointed geometry were manufactured from cemented carbide containing 11% Co and 12% titanium/tantalum/niobium carbides. Such a high cobalt content in cemented carbides is prohibitive in any other known technique developed to promote well-bonded CVD diamond coatings to carbide parts. The average linear thermal expansion coefficient of this carbide material is $6.4 \times 10^{-6} °C^{-1}$ in the 25-1000°C temperature range. Diamond anchoring particles 40μm in size were vacuum brazed to the bur heads at 1040°C for 5 minutes with a braze material containing 7% Cr, 4.5% Si, 3% Fe, 3.2% B, <1% Co, balance Ni. The required closely packed monolayers of diamond particles were firmly attached to the bur heads protruding an average of 20μm above the braze. Comparative samples of the same carbide and geometry but with no brazed anchoring particles were also prepared, and both types of samples were PVD titanium nitrided and CVD diamond coated at 950°C. The resulting diamond layers were 50μm thick.

As in the previous examples, the CVD coatings on the comparative samples having no anchoring diamonds peeled off spontaneously upon cooling from the deposition temperature, whereas samples of the present invention were extensively tested in glass/MACOR® cutting trials, with no measurable weight losses nor observable microscopic changes in the CVD diamond coatings on any of the samples of the present invention.

It is thus demonstrated by the above examples that hard coatings on samples prepared with a protruding particle morphology as described herein exhibit very high bonding strength to their substrates. It has therefore been demonstrated that the present invention does provide a method for promoting strong adherence between a variety of substrate materials and hard coatings by the use of an intermediate layer of outwardly protruding anchoring particles partially embedded in the substrate surface layer.

While the present invention has been illustrated by the description of one or more embodiments thereof, and while the embodiments have been described in considerable detail, there is no intention to restrict or in any way limit the scope of the appended claims to such details. Additional advantages and modifications will readily appear to those skilled in the art. The invention in its broader aspects is therefore not limited to the specific details, representative apparatus and method and illustrative examples shown and described. Accordingly, departures may be made from such details without departing from the scope or spirit of applicant's general inventive concept.

WHAT IS CLAIMED IS:

1. A process for coating a substrate with an adherent hard coating, comprising the steps of:

attaching to a surface layer of a substrate to be coated a distribution of discrete particles that partially extend into the substrate surface layer and partially protrude outwardly from the substrate surface layer; and

coating the substrate surface layer having attached outwardly protruding particles with a hard material.

2. The process of claim 1, wherein the hard material has a Vickers hardness value of greater than about 1,000.

3. The process of claim 1, wherein the hard material is selected from the group consisting of: diamond, carbon nitride, cubic boron nitride, titanium nitride, titanium carbonitride, silicon carbide, and $X_aY_bZ_c$ where X, Y and Z are elements selected from the group consisting of: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn , Fe, Al, Si, C, N, O and B; and a, b and c are non-negative integer numbers.

4. The process of claim 1, wherein the substrate to be coated is comprised of a material selected from the group consisting of: cemented carbide, steel, silicon nitride, Ti/Al/V alloys, Ti/Al/V/Sn alloys, Fe/Ni/Co alloys, Mo, Cu, Ti, W, Ta and Va.

5. The process of claim 1, wherein the discrete particles attached to the substrate surface layer are comprised of a material selected from the group consisting of: natural diamond, synthetic diamond, silicon carbide, silicon nitride, cubic boron nitride, ceramic oxides, metal oxides, reinforced composites, and mixtures thereof.

6. The process of claim 1, wherein the distribution of discrete particles creates a surface density of the outwardly protruding particles of about 50% to about 85% of the substrate surface layer to be coated.

7. The process of claim 1, wherein the discrete particles to be attached to the substrate surface layer have an average size of about 10μm to about 250μm.

8. The process of claim 7, wherein the discrete particles are attached to the substrate surface layer such that about 10% to about 90% of each discrete particle protrudes outwardly from the substrate surface layer.

9. The process of claim 1, wherein the discrete particles are attached by bombarding the substrate surface layer with the particles.

10. The process of claim 9, wherein the substrate surface layer is first softened.

11. The process of claim 9, further comprising coating the substrate surface layer with a volatile adhesive prior to attaching the particles.

12. The process of claim 11, wherein the substrate surface layer is coated with an adhesive selected from the group consisting of: ethylene glycol, methyl cellulose, hydroxypropyl cellulose, polyethylene, polypropylene, polystyrene, and mixtures thereof.

13. The process of claim 1, wherein the discrete particles are attached to the substrate surface layer by mixing the particles with a volatile adhesive, coating the substrate surface layer with the particle-containing adhesive, and vaporizing the adhesive.

14. The process of claim 13, wherein the particles are mixed with an adhesive selected from the group consisting of: ethylene glycol, methyl cellulose, hydroxypropyl cellulose, polyethylene, polypropylene, polystyrene, and mixtures thereof.

15. The process of claim 1, wherein the substrate surface layer is an intermediate binding layer and the discrete particles are attached to the binding layer.

16. The process of claim 15, wherein the intermediate binding layer is applied to the substrate by a method selected from the group consisting of: brazing, plating, chemically depositing, electrochemically depositing, plasma spraying, CVD and PVD.

17. The process of claim 16, wherein the discrete particles are attached to a brazed intermediate binding layer selected from the group consisting of: Ni/Cr alloys, Ag/Cu alloys and Au alloys.

18. The process of claim 1 further comprising coating the substrate surface layer and outwardly protruding particles with a chemical barrier prior to coating with the hard material, wherein the chemical barrier coated particles protrude outwardly from the chemical barrier coated substrate surface layer.

19. The process of claim 18, wherein the chemical barrier is comprised of a material selected from the group consisting of: boron, titanium boride, titanium nitride and titanium carbonitride.

20. The process of claim 18, wherein the chemical barrier is coated to a thickness of about $0.01\mu m$ to about $10\mu m$.

21. The process of claim 1, wherein the hard material is coated to a thickness of less than about $1\mu m$ up to about $300\mu m$.

22. The process of claim 21, wherein the hard material is coated to a thickness between about 30μm and about 150μm.

23. The process of claim 1, wherein the hard material is coated by chemical vapor deposition.

24. A process for coating a substrate with an adherent hard coating, comprising the steps of:

attaching to a surface layer of a substrate to be coated a distribution of discrete particles that partially extend into the substrate surface layer and partially protrude outwardly from the substrate surface layer, the discrete particles comprising a material selected from the group consisting of: natural diamond, synthetic diamond, silicon carbide, silicon nitride, cubic boron nitride, ceramic oxides, metal oxides, reinforced composites, and mixtures thereof; and

coating the substrate surface layer and outwardly protruding particles with a hard material having a Vickers hardness value of greater than about 1,000.

25. A process for making a dental bur having an adherent diamond coating, comprising the steps of:

attaching to a surface to be diamond coated a distribution of discrete particles that partially extend into the surface and partially protrude outwardly from the surface;

coating the surface having attached outwardly protruding particles with a diamond coating by chemical vapor deposition.

26. A dental bur having an adherent diamond coating, comprising:

a substrate;

a plurality of discrete particles partially embedded in the substrate; and

a diamond coating on the discrete particles and the substrate, wherein the discrete particles form a mechanical interlock between the substrate and the diamond coating.

27. The dental bur of claim 26, wherein the substrate is comprised of WC-Co$\leq$6%.

28. The dental bur of claim 26, wherein the discrete particles are comprised of a material selected from the group consisting of: natural diamond, synthetic diamond, silicon carbide, silicon nitride, cubic boron nitride, ceramic oxides, metal oxides, reinforced composites, and mixtures thereof.

29. The dental bur of claim 26, wherein the distribution of discrete particles has a surface density of about 50% to about 85% of the substrate.

30. The dental bur of claim 26, wherein the discrete particles have an average size of about 10μm to about 250μm.

31. The dental bur of claim 30, wherein about 10% to about 90% of each discrete particle is embedded in the substrate.

32. The dental bur of claim 26, wherein the diamond coating has a thickness of less than about 1μm up to about 300μm.

33. The dental bur of claim 26, wherein the diamond coating has a thickness between about 30μm and about 150μm.

34. A dental bur having an adherent diamond coating, said dental bur made by the process of claim 9, and said dental bur comprising:

a substrate;

a plurality of discrete particles partially embedded in the substrate; and

a diamond coating on the discrete particles and the substrate, wherein the discrete particles form a mechanical interlock between the substrate and the diamond coating.

35. A dental bur having an adherent diamond coating, said dental bur made by the process of claim 13, and said dental bur comprising:

a substrate;

a plurality of discrete particles partially embedded in the substrate; and

a diamond coating on the discrete particles and the substrate, wherein the discrete particles form a mechanical interlock between the substrate and the diamond coating.

36. A dental bur having an adherent diamond coating, said dental bur made by the process of claim 17, and said dental bur comprising:

a substrate having a brazed intermediate binding layer thereon;

a plurality of discrete particles partially embedded in the brazed intermediate binding layer; and

a diamond coating on the discrete particles and the brazed intermediate binding layer, wherein the discrete particles form a mechanical interlock between the brazed intermediate binding layer and the diamond coating.

37. A dental bur having an adherent diamond coating, comprising:

a substrate;

a plurality of discrete particles partially embedded in the substrate, wherein the discrete particles have an average size of about 10μm to about 250μm;

a chemical barrier coating on the discrete particles and the substrate, wherein the chemical barrier coating has a thickness of about 0.01μm to about 10μm; and

a diamond coating on the chemical barrier coated discrete particles and substrate having a thickness of less than about 1μm up to about 300μm, wherein the discrete particles form a mechanical interlock between the substrate and the diamond coating.

38. A dental bur having an adherent diamond coating, comprising:

a substrate;

a braze alloy layer on the substrate;

a plurality of discrete particles partially embedded in the braze alloy layer, wherein the discrete particles have an average size of about 10μm to about 250μm;

a chemical barrier coating on the discrete particles and the braze alloy layer, wherein the chemical barrier coating has a thickness of about 0.01μm to about 10μm; and

a diamond coating on the chemical barrier coated discrete particles and braze alloy layer having a thickness of less than about 1μm up to about 300μm, wherein the discrete particles form a mechanical interlock between the braze alloy layer and the diamond coating.

39. A dental bur having an adherent diamond coating, comprising:

a substrate;

a braze alloy layer on the substrate;

a plurality of discrete particles partially embedded in the braze alloy layer, wherein the discrete particles have an average size of about 10μm to about 250μm; and

a diamond coating on the discrete particles and the braze alloy layer having a thickness of less than about 1μm up to about 300μm, wherein the discrete particles form a mechanical interlock between the braze alloy layer and the diamond coating.

40. An article having an adherent hard coating, comprising:

a substrate;

a plurality of discrete particles partially embedded in the substrate; and

a hard coating on the discrete particles and the substrate, wherein the discrete particles form a mechanical interlock between the substrate and the hard coating.

41. The article of claim 40, wherein the hard coating is comprised of a material selected from the group consisting of: diamond, carbon nitride, cubic boron nitride, titanium nitride, titanium carbonitride, silicon carbide, and $X_aY_bZ_c$ where X, Y and Z are elements selected from the group consisting of: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn , Fe, Al, Si, C, N, O and B; and a, b and c are non-negative integer numbers.

42. The article of claim 40, wherein the substrate is comprised of a material selected from the group consisting of: cemented carbide, steel, silicon nitride, Ti/Al/V alloys, Ti/Al/V/Sn alloys, Fe/Ni/Co alloys, Mo, Cu, Ti, W, Ta and Va.

43. The article of claim 40, wherein the discrete particles are comprised of a material selected from the group consisting of: natural diamond, synthetic diamond, silicon carbide, silicon nitride, cubic boron nitride, ceramic oxides, metal oxides, reinforced composites, and mixtures thereof.

44. The article of claim 40, wherein the distribution of discrete particles has a surface density of about 50% to about 85% of the substrate.

45. The article of claim 40, wherein the discrete particles have an average size of about 10μm to about 250μm.

46. The article of claim 45, wherein about 10% to about 90% of each discrete particle is embedded in the substrate.

47. The article of claim 40, wherein the hard coating has a thickness of less than about 1μm up to about 300μm.

48. The article of claim 40, wherein the hard coating has a thickness between about 30μm and about 150μm.

49. The article of claim 40, wherein the article is a dental article selected from the group consisting of: file, plier, cutting wheel, abrasive wheel and drill.

50. The article of claim 40, wherein the article is a dental implant.

51. The article of claim 40, wherein the article is selected from the group consisting of: file, cutter, marker, drill and engraving tool used on jewelry and glass.

52. The article of claim 40, wherein the article is a medical article selected from the group consisting of: knives, scalpels and bone implants.

53. The article of claim 40, wherein the article is selected from the group consisting of: extruding die, drawing die, indexable insert, drill, tap, reamer, cutting wheel, cutting stone, abrasive wheel and abrasive stone used for forming and cutting metal and wood.

54. The article of claim 40, wherein the substrate is a wear resistant surface on an article selected from the group consisting of: micrometer, calliper, bearing, nozzle and wire transport guide.

55. The article of claim 40, wherein the article is an electronic component.

56. The article of claim 40, wherein the article is a space bound device.

57. An article having an adherent diamond coating, comprising:

a substrate;

a metal binder layer on the substrate;

a plurality of discrete particles partially embedded in the binder layer;

a chemical barrier coating on the discrete particles and the binder layer; and

a diamond coating on the chemical barrier coated discrete particles and binder layer,

wherein the discrete particles are of a size sufficient to protrude outwardly from the binder layer to provide mechanical anchoring for the diamond coating to the substrate and binder layer, and

wherein the chemical barrier coating has a thickness sufficient to substantially prevent harmful chemical interactions between the diamond coating and the substrate and binder layer.

58. The article of claim 57, wherein the metal binder layer includes nickel.

59. The article of claim 58, wherein the substrate includes tungsten carbide.

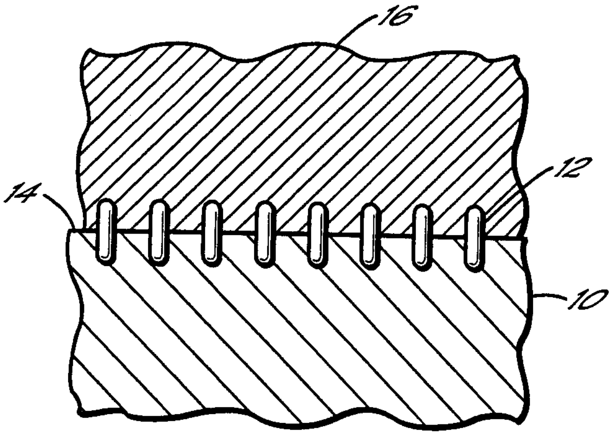


FIG. 1

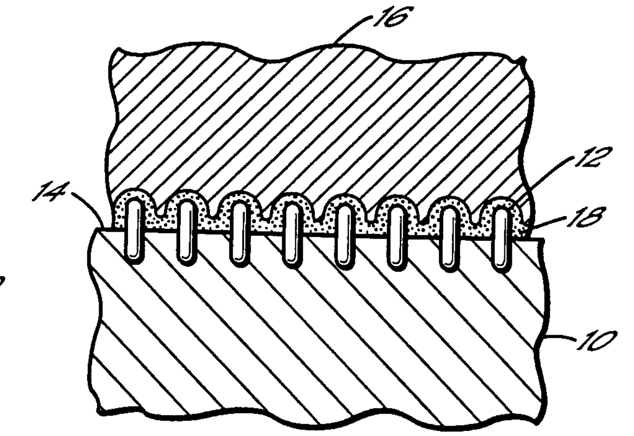


FIG. 2

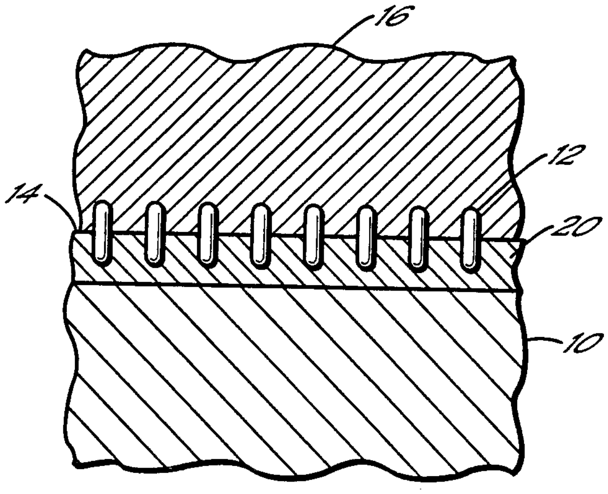


FIG. 3

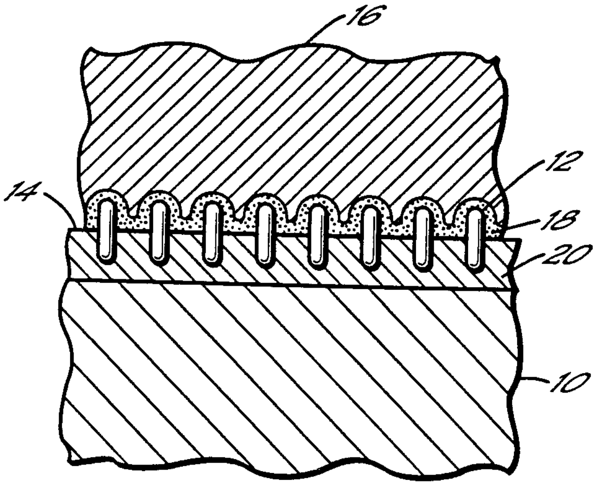


FIG. 4

INTERNATIONAL SEARCH REPORT

Inter nal Application No
PCT/US 00/26710

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C28/00 C23C30/00 C23C16/02 A61C3/02

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C23C A61C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

PAJ, WPI Data, EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search
17 January 2001

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INTERNATIONAL SEARCH REPORT

Inter… …nal Application No
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