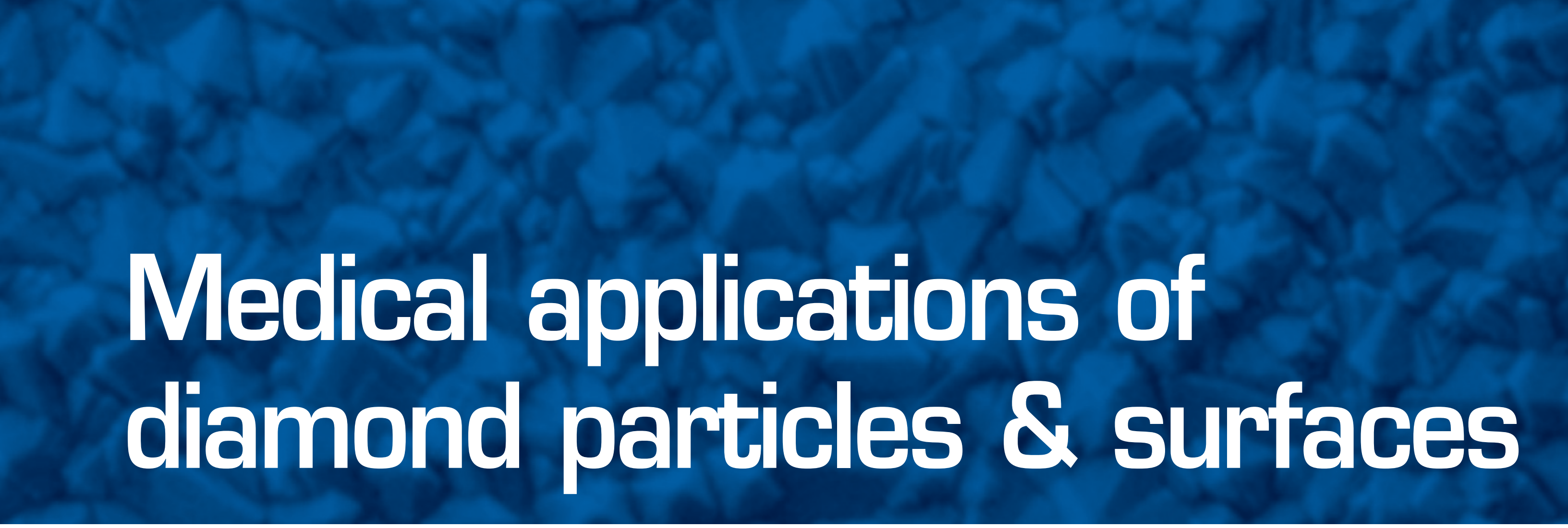

Medical applications of diamond particles & surfaces

Diamond has been considered for use in several medical applications due to its unique mechanical, chemical, optical, and biological properties. In this paper, methods for preparing synthetic diamond surfaces and particles are described. In addition, recent developments involving the use of diamond in prostheses, sensing, imaging, and drug delivery applications are reviewed. These developments suggest that diamond-containing structures will provide significant improvements in the diagnosis and treatment of medical conditions over the coming years.

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Diamond is an allotrope of carbon that is being considered for use in several medical applications[1]. Ramachandran determined that the crystal structure of diamond consists of two close packed interpenetrating face centered cubic lattices; one lattice is shifted with respect to the other along the elemental cube space diagonal by one-quarter of its length[2]. If one approximates carbon atoms as equal diameter rigid spheres, the filling of this construction is 34 %[3]. Due to the carbon-carbon distance (1.54 Å), diamond crystal exhibits the highest atomic density (1.76 x 10^{23} cm^{-3}) of any solid. The very high bond energy between two carbon atoms (83 kcal/mol) and the directionality of tetrahedral bonds are the main reasons for the high strength of diamond. Diamond demonstrates the highest Vickers hardness value of any material (10 000 kg/mm^{2}). The tribological properties of diamond are also impressive; the coefficient of friction of polished diamond is 0.07 in argon and 0.05 in humid air. Diamond is resistant to corrosion except in an oxygen atmosphere at temperatures over 800 °C. In addition, type IIa diamond exhibits the highest thermal conductivity of all materials (20 W cm^{-1} K^{-1} at room temperature).

Growth of synthetic diamond

The graphite-diamond transformation at thermodynamic equilibrium necessitates the use of very high temperatures and pressures. Bundy *et al.* at General Electric developed a high pressure-high temperature approach for creating diamond from graphite in the 1950s[4]. This technique creates small diamond crystals that are commonly utilized for polishing, cutting, and grinding. Growth of diamond coatings at low pressure using hydrocarbon pyrolysis was first reported by Eversole *et al.* at Union Carbide in 1962[5]. In the late 1960s and early 1970s, Derjaguin *et al.* and Angus *et al.* introduced the concept of activating a mixture containing hydrogen and a hydrocarbon gas for low-pressure chemical vapor deposition of diamond coatings[6,7]. For example, Angus *et al.* demonstrated deposition of diamond layers on natural diamond powder by thermal decomposition of methane at a temperature of 1050 °C and a pressure of 0.3 Torr[7]. In these methods, diamond coatings are grown

ISSN:1369 7021 © Elsevier Ltd 2011.

from an activated gas phase; this phase contains hydrogen (~99 %) as well as methane or other carbon-containing gases. Activation of the gas commonly involves the use of a hot filament, combustion flame, plasma, or a combination of these approaches. Diamond coatings are formed by the decomposition of activated hydrocarbon species into excited carbon atoms. Diamond coatings are commonly deposited on metallic substrates for minimizing wear, corrosion, and metal release; for example, a diamond-coated metallic implant will behave mechanically as the metallic substrate and chemically as the diamond coating.

Several parameters must be considered in deposition of microcrystalline diamond coatings. Hydrogen serves several roles, including termination of carbon dangling bonds, stabilization of diamond clusters, removal of sp^2-hybridized carbon from the surface, and abstraction of hydrogen from carbon-hydrogen bonds on the surface[8]. The chemical properties of the substrate regulate the structure of the diamond coating[9]. Diamond coating growth on cobalt, ferrous alloys, and nickel alloys is challenging because the nucleation of diamond is hindered by high carbon diffusion rates within these materials[10]. Formation of graphite is commonly observed on nickel and other elements that contain partially-filled electron shells.

Growth of microcrystalline diamond on non-diamond surfaces involves scratching of the substrate to promote diamond nucleation and/or use of an interlayer between the diamond coating and the non-diamond substrate. Ultrasonic seeding of the substrate with ultradispersed detonation diamond has also been used to increase the nucleation of diamond[11,12]. It should be noted that scratching may alter the surface in a poorly-defined manner; non-uniform features may limit use of the coated material in medical applications. In addition, heterogeneous films containing diamond and graphitic carbon may be created on substrates that are scratched with diamond paste[10].

An interlayer material (e.g., titanium nitride, aluminum nitride, and tungsten carbide) can promote diamond nucleation and facilitate coating adhesion through relief of interfacial stresses[13]. Properties of the interlayer material include: a similar thermal expansion coefficient value to that of diamond for reducing thermal stresses; low diffusivity of carbon for increasing diamond nucleation; and small lattice mismatch with diamond as well as with the bulk material. Silicon nitride is frequently utilized as a bulk material due to the fact that it exhibits a low coefficient of thermal expansion. In addition, silicon nitride exhibits high fracture toughness and high hardness values[14,15]. Furthermore, silicon nitride is compatible with diamond CVD deposition temperatures (650 – 1000 °C).

Significant academic and industrial research activities are underway to create nanocrystalline diamond coatings. The term nanocrystalline diamond is utilized for describing materials that contain grain sizes below 100 nm, usually 10 – 100 nm (Fig. 1)[16]. The mechanism for nanocrystalline diamond growth, which involves a hydrogen-rich growth chemistry, is similar to that for microcrystalline diamond or polycrystalline diamond growth. Competitive crystal growth results in a columnar texture that is oriented in the growth direction and the coarsening of grain sizes with film thickness (van der Drift growth). By controlling the initial nucleation density and the growth parameters, one can limit re-nucleation density and maintain grain sizes from 10 to 100 nm for nanocrystalline diamond films up to a few micrometers in thickness. When film thickness exceeds a few micrometers, nanocrystalline diamond growth behaves like microcrystalline diamond growth; in this situation, roughness increases with film thickness.

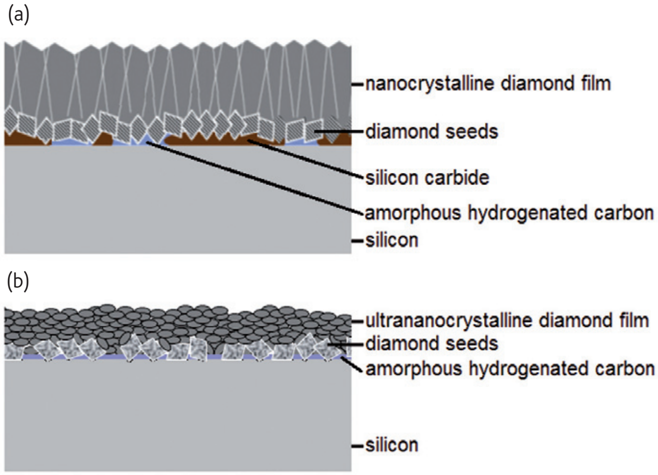

Fig. 1 Schematic explaining the possible nucleation mechanisms of (a) nanocrystalline diamond and (b) ultrananocrystalline diamond. Reproduced with permission from[16]. © Wiley-VCH Verlag GmbH & Co. KGaA.

Nanocrystalline diamond coatings exhibit small crystallite sizes; these materials are considered to be appropriate for tribological applications due to their relatively smooth surfaces. Amaral *et al.* examined the wear behavior of nanocrystalline diamond; steady-state friction coefficients of 0.01 – 0.05 in unlubricated environments and water-lubricated environments were observed[17]. The wear rate under water lubrication was 1.9×10^{-10} mm^3 N^{-1} m^{-1}; testing in Hank's balanced salt solution revealed similar friction (0.06) and wear data. Testing in dilute fetal bovine serum revealed a higher coefficient of friction (0.10); this finding was associated with protein attachment. Wear behavior in Ringer's solution and synthetic serum was impressive; final wear rates of $\sim 10^{-10}$ mm^3 N^{-1} m^{-1} were obtained.

The term ultrananocrystalline diamond was coined by researchers at Argonne National Laboratory to distinguish their form of diamond from other forms of diamond on the basis of grain size. Ultrananocrystalline diamond contains grains with sizes below 10 nm, usually between 2 and 5 nm. 95 – 98 % of the material, in the form of sp^3-hybridized carbon, is found in these grains; the remaining material, in the form of sp^2-hybridized carbon, resides at atomically abrupt grain boundaries[18,19]. Ultrananocrystalline diamond films are produced in an argon-rich, hydrogen-deficient environment using microwave plasma-enhanced chemical vapor deposition. Films grown from plasmas containing ~99 % argon and ~1 % methane are able to grow directly on SiO_2 since carbon dimers (C_2) form a silicon carbide nucleation layer. Work by Sumant *et al.* and Naguib *et al.* has indicated that a tungsten