Diamond & Related Materials 21 (2012) 50–57

Contents lists available at SciVerse ScienceDirect

Diamond & Related Materials

journal homepage: www.elsevier.com/locate/diamond

Tribochemical polishing CVD diamond film with FeNiCr alloy polishing plate prepared by MA-HPS technique

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ARTICLE INFO

Article history:
Received 1 September 2011
Accepted 11 October 2011
Available online 20 October 2011

Keywords:
Tribochemical polishing
CVD diamond film
Material removal mechanism
Polishing plate
Mechanical alloying
Hot-press sintering

ABSTRACT

A novel polishing plate is most important for tribochemical polishing (TCP) diamond. This paper investigated the mechanisms of TCP and pointed out the requirements for the polishing plate. Unpaired d electrons, vertical aligned principle, high hardness and oxidation resistance at elevated temperature were general requirements for polishing plate. Based on these requirements, FeNiCr alloy polishing plate was prepared by the combination technique of mechanical alloying and hot-press sintering. Optical microscope, scanning electron microscope, Talysurf surface profiler, X-ray diffraction, electron probe microanalysis and Raman spectroscope were employed to characterize the prepared polishing plate and identify the removal mechanism. It was found that FeNiCr alloy polishing plate had higher hardness and oxidation resistance than stainless steel 304 and cast iron. FeNiCr alloy polishing plate obtained a material removal rate of 3.7 μm/min, which was higher than that of stainless steel 304 plate, cast iron plate and TiAl alloy plate. The mechanism for TCP can be described as converting diamond into graphite through friction heating and the interaction of the diamond with a catalytic metal disk; the catalytic metal acted on the diamond surface by means of their unpaired d electrons. If the metal structure of polishing plate was suitable to vertically bond with several carbon atoms on diamond surface, diamond would tend to convert into graphite more easily. Finally the non-diamond carbon was removed by mechanical friction, oxidation and diffusion into metal disk.

1. Introduction

Diamond possesses excellent physical, thermal and chemical properties, such as the highest hardness (100 Gpa), chemically inert, high thermal conductivity ($2\times10^3 Wm^{-1} K^{-1}$), elasticity modulus ($1.04\times10^{12}$ Pa), electrical resistance ($>10^{13}\Omega$ cm), electronic gap (5.45 eV), wide-range transparency (from ultraviolet to far infrared) and a low friction coefficient, however it has not been used widely due to its high cost and scarcity [1]. Fortunately, the debut of CVD diamond greatly expands the application field of diamond from the traditional to the fields of optical, thermal, electronic semiconductors, acoustics, and so on [2]. For example, the combination of strength, high thermal conductivity and chemical inertness makes CVD diamond a compelling choice for far infrared window material in extreme environments, such as very high power CO_2 laser exit windows and missile domes [3,4]. High thermal conductivity and electrical resistance enable CVD diamond to be used as heat-spreading substrates for high-power density ICs [5]. However, the columnar growth of CVD diamond results in a polycrystalline nature and the grain sizes increase with film thickness [6]. Therefore, if CVD diamond films could be used in these fields, it is extremely important for the surface to be planar and highly polished.

Encouragingly, people have long been aware that the wear on diamond tools is more serious when machining iron or nickel than other materials such as copper and aluminum, because metals such as iron or nickel are effective carbon solvent. They can etch diamond at elevated temperatures [7–9]. So these materials could be used to polish diamond. Therefore, recently, many experts have used iron, stainless steel, nickel and cast iron plate to polish diamond by thermochemical technique and confirmed that these materials indeed have a high polishing rate [10–13]. By this technique, the surface material of diamond is removed by sliding on the iron plate at a temperature of 1000–1200 K and under the pressure of 0.05–1 MPa [14,15]. In order to reduce the oxidation of the polishing plate, the polishing experiments must be carried out in pure hydrogen or a hydrogen-containing atmosphere, therefore, complex devices for gas transmission are needed; also, the metal plates will soften and deform at high temperature, which leads to low material removal rate and poor surface flatness.

In order to solve these problems, tribochemical polishing technique (TCP) has been developed (also called dynamic friction polishing, DFP) [16–19]. By this method diamond is polished through being simply pressed against a metal plate rotating at a high speed (the linear velocity is 12–25 m/s and the pressure is 3–7 Mpa). It utilizes the

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doi:10.1016/j.diamond.2011.10.015

thermochemical reaction occurring as a result of dynamic friction between diamond and plate in the atmosphere. Compared with the thermochemical technique, the tribochemical polishing technique is a more practical technique because it is free of the heavy heating equipment and the complex ventilation equipment and reduces the deformation of the plate by using local contact in place of the overall heating. It is one of the most promising methods which developed in recent years appropriate for polishing single crystal or CVD diamond with high efficiency and low cost.

In the diamond polishing process, the commonly used plate materials are iron, stainless steel, cerium, nickel, cobalt, titanium and other transition element materials. However, lower hardness, poor oxidation resistance at high temperature and poor wear resistance of these existing materials make them wear out easily and become deformed in the diamond polishing process, and adhere easily to the surface of diamond films. These would seriously impact the surface quality and accuracy of the polished diamond films. Therefore, a kind of polishing plate with good properties becomes even more important for diamond planarization.

In this paper, the requirements for polishing plate in TCP are discussed based on the polishing mechanisms. Then a new polishing plate was prepared by the combination technique of mechanical alloying and hot-press sintering and it was applied to finish the diamond film by TCP technique. After polishing, the compositions of polished diamond surface and polishing plate were investigated.

2. Requirement for polishing plate in TCP

In TCP process of diamond films, many factors influences diamond removal, including temperature, pressure, friction, metal catalyst, diffusion and oxidation. Iron [20], stainless steel [21], cerium [22], nickel [23], manganese [24], titanium [25] and copper [26] are usually used to polish diamond. But the material removal rates with these materials are different. In order to prepare good polishing plate, the mechanisms for TCP should be investigated.

Many theories are introduced to investigate the mechanism of TCP, including metal-catalyzed reaction [27], fracture-based wear mechanism [28], energy-dissipation mechanism [29], pressure-introduce phase transformations mechanism [30], thermal mechanism of wear, diffusion and oxidation mechanism [31,32]. Among them, the metal-catalyzed reaction theory may be presented to explain material removal mechanism of diamond TCP. It could explain the reason why Fe, Co, Mn, Ce, Ni have a higher diamond wear rate or diamond removal rate than do Cu, Al, Mg. It indicates that catalytic metals play an important role in TCP process.

Ed Paul [27] attempted to investigate the relationship between catalytic metal and diamond tool wear by analyzing the metal electronic structure. He maintained that diamond tool wear had certain relationship with the number of the unpaired d electrons. More unpaired d electrons resulted in a faster tool wear rate; likewise, fewer unpaired d electrons led to a slower wear rate. As can be seen from the data of commonly used metals in Table 1, Ce, La, Mn, Ni, Co, Fe, Ti, Cr, Mo, W have unpaired d electrons which would result in diamond tool wear when machining. In contrast, Zn, Mg, Al, Ag, Au have no unpaired d electrons, which can be machined by diamond tools, but very few of these materials are used for diamond processing. Therefore, the unpaired d electrons may be the driving force for the diamond graphitization and diamond removal.

So how do the unpaired d electrons act on diamond? The unpaired d electrons may chemically bond with diamond carbon. The force of chemical bond may drive the carbon in diamond surface to move and be converted to graphite. However, the action of a single metal atom is insignificant for diamond conversion. If the atoms in the same metal cell act on several adjacent diamond carbon atoms, it may be sufficient for diamond conversion. Therefore, in the TCP process, not only should the metal have unpaired d electrons, but also should have correspondingly aligned atoms to form vertical bonds so that the metal could have a concentrated effect on the diamond. For example, nickel is face-centered cubic structure. The edge length of the equilateral triangle formed by the three adjacent atoms on Ni's (111) surface is 2.49 Å, which is very close to that of diamond's three atoms (2.51 Å). Therefore, Ni atoms can vertically align with diamond atoms.

As shown in Fig. 1, three atoms a, b and c in Ni (111) surface, respectively, are vertically aligned with the diamond atoms 1′, 2′, 3′. With two unpaired d electrons, the three nickel atoms a, b and c can concentratively act on three diamond atoms, which convert the diamond's atomic structure into graphite's hexagonal structure (the inner triangle edge length is 2.46 Å).

By the same token, when the distance between atoms in the diamond-type structure (111) face, the face-centered cubic structure (111) face as well as the close-packed hexagonal structure (0001) face is equal to or close to 2.51 Å, it meets the vertical alignment principle [33]. In accordance with this principle, Fe with 4 unpaired d electrons and Cr with 5 unpaired d electrons can also be transformed into face-centered cubic structure at high temperature. The edge lengths of the equilateral triangle formed by the three adjacent atoms on Fe's and Cr's surfaces are respectively 2.52 Å and 2.56 Å. Being similar with Ni, they can concentrately act on diamond's atoms. Therefore, Fe and Cr can also be used to polish diamond. Co with 3 unpaired d electrons is close-packed hexagonal structure. The distance between hexagon structured atoms on its (0001) face is 2.50 Å, which is closer to 2.51 Å than Ni atoms (2.49 Å) and iron atoms (2.52 Å). Therefore theoretically, Co is more suitable for diamond polishing. Similarly, diamond can be also be polished by metals such as Pt, Mn, Pd, Ce, Mo, W, La, Ti and alloys such as Ni-Cr, Ni-Fe, Ni-Co, Ni-Mn, Co-Cr, Ni-Fe-Mn, Fe-Ni-Cr, etc.

Actually, these metals are just the catalytic agents in the synthesis of diamond. When Ni-Cr-Fe, Mn-Cu, Co, Mn-Co, Ni, Fe and Mn act as catalyst, the synthesis pressure and temperature are relatively low.

Table 1
Data for elements with diamond turning properties.

Without unpaired d electrons				With unpaired d electrons			
Element		Electron configuration	No. of unpaired d-shell electrons	Element		Electron configuration	No. of unpaired d-shell electrons
Zn	Zinc	$3d^{10}4s^2$	0	Ce	Cerium	$4f^1 5d^1 6s^2$	1
Mg	Magnesium	$3\ s^2$	0	La	Lanthanum	$5d^1 6s^2$	1
Al	Aluminum	$3p^1$	0	Mn	Manganese	$3d^5 4s^2$	5
Ge	Germanium	$4s^2 4p^2$	0	Ni	Nickel	$3d^8 4s^2$	2
Ag	Silver	$4d^{10}5s^1$	0	Co	Cobalt	$3d^7 4s^2$	3
Au	Gold	$5d^{10}6s^1$	0	Fe	Iron	$3d^6 4s^2$	4
Cu	Copper	$3d^{10}4s^1$	0	Ti	Titanium	$3d^2 4s^2$	2
Si	Silicon	$3s^2 3p^1$	0	Cr	Chromium	$3d^5 4s^1$	5
				V	Vanadium	$3d^3 4s^2$	3
				Mo	Molybdenum	$4d^5 5s^1$	5
				W	Tungsten	$5d^4 6s^2$	4
				Pt	Platinum	$5d^9 6s^1$	1