

## **Chapter 7**

# **Theoretical Study of Material Removal Mechanism**

### **7.1 Introduction**

From Chapters 5 and 6, it is known that during dynamic friction polishing of PCD composites, the interface temperature increases dramatically due to frictional heating. The elevated temperature and contact with a catalytic metal stimulates the diamond on the specimen surface and converts it to other forms of carbon, which are then mechanically /chemically removed. As can be seen, phase transformation and chemical reactions of carbon at elevated temperatures play an important role during polishing. A comprehensive study of these interface reactions, including chemical reaction of carbon with metal, carbon phase transformation, oxidation of carbon and diffusion of carbon into metal disk, appears to be very essential.

The aim of the chapter is to obtain a comprehensive understanding of the polishing mechanism by theoretical study of the thermodynamics and chemical kinetic of these interface reactions, their reaction mechanisms, condition and probability. This chapter will

combine the theoretical study with experimental results from Chapter 5 to discuss and summarize the material removal mechanisms and the associated chemical reactions in the dynamic friction polishing process.

## 7.2 Reaction of Carbon with Transition Metals

Carbon can react with transition metals in many ways. The ability for a transition metal to react with carbon increases with the number of electron vacancies in its *d*-orbital [Sung, C. M. and Tai, 1997]. A transition metal tends to react with carbon by overlapping its *d*-orbital with carbon's *p*-orbital. Hence, the reactivity of a transition metal toward carbon is primarily determined by its electronic state, specifically, the number of electron vacancies of its *d*-orbital. As a result, the reactivity of transition metals generally decreases in the order of groups: IIIB, IVB, VB, VIA, VIIB, VIIIB, IB and IIB. Thus, elements (e.g. Cu, Zn) with no *d* vacancies show little interaction with carbon, and are inert relative to carbon. Elements (e.g. Fe, Co) with few *d*-vacancies exhibit moderate interaction, and are effective carbon solvents. Elements (e.g. Ti, V) with many *d*-vacancies manifest strong interaction, and are carbide formers, tending to lock up carbon in carbides. Transition metals with intermediate reactivity can attract carbon atoms in graphite without forming carbide. They can act as a catalyst for the graphite  $\leftrightarrow$  diamond transition, and drastically increase the transition rate in either a forward (in diamond stability field) or a backward direction (in graphite stability field).

The increasing reactivity between metal and carbon is also reflected in the increasing solubility of carbon in metal. However, the trend of increasing solubility with the increasing number of *d*-vacancies tends to peak in iron group metals and then decline. The reverse in solubility with further increases in the number of *d*-vacancies is due to the over-reaction between metal and carbon. As the reactivity exceeds a threshold value, carbon atoms begin to lose their mobility in the solution. They are eventually locked up in the structure as carbide.

Iron is the most dominant catalyst that is used today for commercial production of diamond under high pressure. General Electric scientists in 1950s [Bovenkerk *et al.*, 1959, Bundy *et al.*, 1955] discovered that certain molten metals could catalyse the formation of diamond under high pressure. These metals contain at least one of a dozen transition metals. These metals are primarily group VIII B (iron group) elements (Fe, Co, Ni, Ru, Rh, Pd, Os, Ir and Pt), but they also include three other transition metals (Mn, Cr, and Ta). These conventional catalysts appear to have a moderate degree of reactivity toward carbon. If the reactivity is too strong, carbon is locked up in carbide instead of forming diamond. On the other hand, if the reactivity is too low, graphite will remain intact and there is no diamond formed, either. The catalytic action relies on the balance of interaction. However, this balance is dependent on temperature [Sung, C.M. *et al.*, 1995/96]. Thus, with increasing temperature, certain metals (e.g. Cu) that are relatively inert toward carbon may become active and, hence, they may exhibit catalytic power.

The most powerful catalysts are Co, Fe, Mn, Ni, and Cr [Sung, C. M. and Tai, 1997]. These elements are major alloying components of catalysts used for the commercial

production of synthetic diamond under high pressure. These elements can also catalyse the conversion of diamond to graphite at low pressure at temperatures above 700 °C. The catalytic reaction appears to be a double-edged sword. An effective catalyst cannot only catalyse the graphite→diamond transition in the stability field of diamond under high pressure, but also catalyse the diamond→graphite transition (back conversion of diamond) in the stability field of graphite at low pressure.

If a diamond tool is used to machine transition metals, the frictional force would increase with an increasing number of *d*-vacancies in the metal [Sung, C. M. and Tai, 1997]. This will in turn increase the temperature during cutting. Cutting at high temperatures can trigger the chemical wear (oxidation, dissolution, graphitization or carbide formation) of diamond. In addition, it has been found that when grinding or machining ferrous metals with diamond tools, the dominating wear mechanism of diamond is graphitization of diamond and it is accelerated by the thermally activated catalytic reaction of iron and ambient oxygen [Ikawa, 1971, Shimada *et al.*, 2004, Tanaka and Ikawa, 1973, Thornton and Wilks, 1979, 1980, Uemura, 2001, Wilks and Wilks, 1994].

As can be seen, under dynamic friction polishing conditions, owing to high temperatures at the diamond–metal interface, structure transformation of carbon (e.g. graphitization of diamond) likely happens, and probably is the dominating polishing mechanism.

### 7.3 Structural Transformation of Carbon

There are several types of carbon lattice structure, including graphite, amorphous carbon, diamond, fullerenes and lonsdaleite [Malshe *et al.*, 1999, Pierson, 1993]. From Bundy's pressure-temperature (P-T) phase transformation diagram for carbon [Bundy *et al.*, 1996] as shown in Fig.7.1, the straight solid line, so-called Berman-Simon line (B-S line) represents equilibrium phase boundaries: above the line diamond is the stable carbon allotrope, while graphite is stable below the line. Region A is the commercial synthesis of diamond from graphite by catalysis. Region B on the dashed line marks the temperature-pressure threshold of very fast solid-solid transformation of graphite to diamond. Region C is the pressure/temperature threshold of very fast transformation of diamond to graphite.

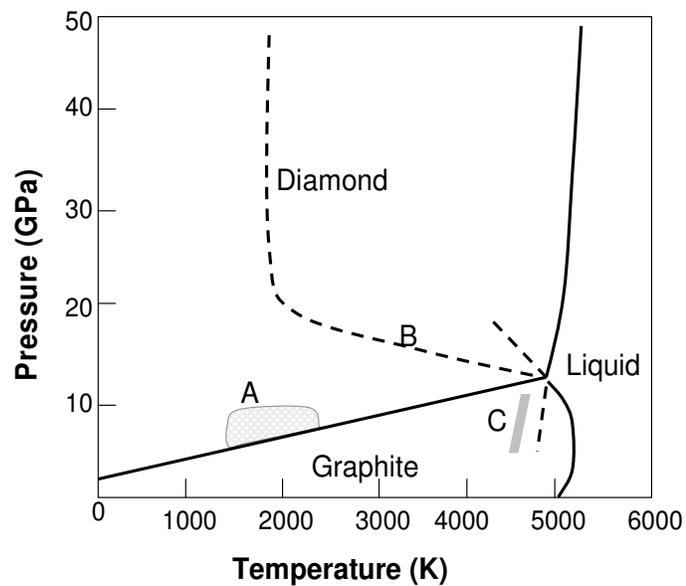


Fig.7.1 P-T phase and transformation diagram for carbon [Bundy *et al.*, 1996]

From the P-T phase diagram of carbon, thermodynamics indicates that diamond is a metastable phase of carbon at room temperature and pressures, and should convert to graphite. However, the reaction rate (kinetics) is so slow that the change is normally undetectable. Increased temperatures will accelerate its conversion to graphite [Hall, 1961, Howes, 1962]. This fast conversion occurs only at elevated temperatures because of a high activation barrier of this phase transition.

The activation barrier of the phase transition can be depicted clearly by an energy diagram. Figure 7.2 shows an energy diagram for the conversion between diamond and graphite. Generally, more stable materials have lower potential energies. Graphite that is more stable is placed lower on the diagram (at lower potential energy) while the less stable diamond (higher potential energy compounds) is higher on the diagram. The binding energy between atoms of carbon is very large (e.g. the cohesive energy of diamond is 717 kJ/mol) [Bundy *et al.*, 1996]. Once carbon atoms are locked into a given phase configuration, typically a large amount of activation energy is required to produce a different stable phase. In order to transfer diamond to graphite, a high-energy barrier must be passed over. The top of this barrier is called the transition state, which represents the highest energy structure involved in the reaction. At the transition state, some of the C-C bonds are stretched and the carbon atoms are beginning to arrange into the planes of graphite [1996]. These planes will be buckled due to stretched bonds between the ultimately non-bonded planes of carbon atoms of graphite. As a result the stabilization afforded by four single C-C bonds at each C atom has begun to be lost, but the resonance stabilization of graphite has not been fully realized.

As a result the C-C bonds in the transition state on average are weaker than the bonds of either diamond or graphite. Thus, the potential energy of the transition state is greater than that of reactant and product.

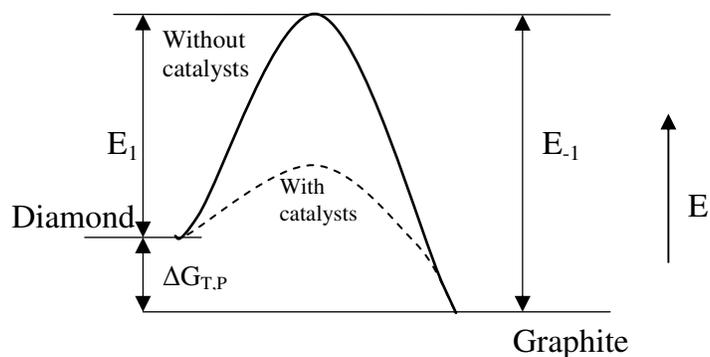


Fig.7.2 Energy diagram for conversion of diamond to graphite

The energy difference between the starting material (diamond) and the transition state is the activation energy. The value of the activation energy depends on the direction of the reaction; the activation energy for the diamond to graphite transformation  $E_1$  is lower than that for the graphite to diamond  $E_{-1}$ . If the activation energy for a reaction is high, the reaction will occur slowly. The rate of reaction is determined by how frequently the atoms collect enough energy to “climb” over the hill, so the higher the barrier the slower the reaction. Also, increasing the temperature, or kinetic energy of the atoms, will increase the reaction rate because the atoms will collect the energy needed to ‘climb’ the barrier more frequently. Much energy in the form of high temperature is needed to convert diamond to transition state so that graphite can be formed. Moreover, catalytic metal can lower the

activation energy and increase the kinetics of the reaction, though the catalysts do not affect the thermodynamics (in Fig.7.2).

In the principle of thermodynamics, the phase transformation is promoted by the difference of the free energies; the phase transformation is determined quantitatively by the probability of the carbon atoms crossing a potential barrier of intermediate state [Wang and Yang, 1999, Zhang *et al.*, 1994]. The Gibbs free energy  $G_{T,P}$  is an adaptable measure of the energy of a state in phase transformation among the competing phases.  $G_{T,P}$  of a phase can be expressed as a function of the pressure-temperature condition and is determined by a general coordinate. The probability of the phase transformation from the metastable phase to the stable phase is determined not only by the Gibbs free energy difference

$$\Delta G_{T,P} = G_{T,P(\text{products})} - G_{T,P(\text{reactants})}, \quad (7.1)$$

but also by the activation energy (see Fig.7.2),

$$E_1 = E_{-1} - \Delta G_{T,P}, \quad (7.2)$$

where  $E_1$  and  $E_{-1}$  are the activation energies for transformation of diamond to graphite and the reverse reaction respectively. The activation energy is necessary for the transition. The rate of the diamond to graphite transition depends on  $E_1$  and the rate of the reverse reaction depends on  $E_{-1}$ . When the two phases are at equilibrium condition,  $\Delta G_{T,P} = 0$ , hence  $E_1 = E_{-1}$ .

Thermodynamically,  $\Delta G_{T,P}$  varies with pressure at a given temperature and is given by

$$(\partial \Delta G_{T,P} / \partial P)_T = \Delta V$$

$$\text{Or } \Delta G_{T,P} = \Delta G_T^0 + \int_0^P \Delta V dp \quad (7.3)$$

where  $\Delta V$  is the volume difference between graphite and diamond, and  $\Delta G_T^0$  is the molar Gibbs free energy difference at zero pressure. When the conditions are at the diamond-graphite phase equilibrium B-S line, the equilibrium criterion takes the form [Leshchuk, 2002]

$$\Delta G_T^0 + \int_0^{P_{eq}} \Delta V dp = 0. \quad (7.4)$$

$$\Delta G_{T,P} = \Delta G_T^0 + \int_0^P \Delta V dp = \Delta G_T^0 + \int_0^{P_{eq}} \Delta V dp + \int_{P_{eq}}^P \Delta V dp = \int_{P_{eq}}^P \Delta V dp \quad (7.5)$$

Also, at the equilibrium condition, P and T satisfy the relation [Berman, 1996, Kennedy and Kennedy, 1976]

$$P_{eq} = 2.73 \cdot 10^6 T + 7.23 \cdot 10^8 \quad (7.6)$$

where  $P_{eq}$  is pressure at equilibrium state, note that  $P_{eq}$  is in Pa. Experimental results [Berman, 1996, Kennedy and Kennedy, 1976, Wang and Yang, 1999] have showed that  $\Delta V$  remains approximately constant ( $\Delta V = 1.7 \times 10^{-6} \text{ m}^3/\text{mol}$ ) with the pressure-temperature condition. It is noticed that at given temperature  $P < P_{eq}$  (at graphite stable field as in Fig.7.1). Thus,  $\Delta G_{T,P}$  for the diamond to graphite transition is given by

$$\Delta G_{T,P} = \Delta V (P - P_{eq}) = 1.7 \cdot 10^{-6} (2.73 \cdot 10^6 T + 7.23 \cdot 10^8 - P) \quad (7.7)$$

From this equation (7.7) and Fig.7.1,  $\Delta G_{T,P}$  for the diamond to graphite transition will increase with increasing temperature and decreasing pressure, and diamond is more unstable at higher temperature and lower pressure.

From reaction kinetics, the rate of transformation of diamond to graphite  $R_g$  is

$$R_g = k_I [C_{diamond}], \quad (7.8)$$

where  $[C_{diamond}]$  is concentration of diamond and  $k_I$  is the rate constant at given temperature. But  $k_I$  is also a function of temperature, according to Arrhenius equation,

$$k_I = A_I \exp(-E_a/RT), \quad (7.9)$$

where  $R$  is gas constant (8.31 J/mol.K),  $A_I$  is a constant known as the frequency factor,  $E_a$  is the activation energy.

In the solid-solid condition transformation between diamond and graphite, the concentration of diamond and graphite  $[C_{diamond}]$  and  $[C_{graphite}]$  can be taken as constant, so the transfer rate is

$$R_g = A_g \exp(-E_a/RT) \quad (7.10)$$

where  $A_g$  is constant.

In the process of synthesizing diamond with catalyst-solvent fluid metal in region A in Fig.7.1, the activation energy  $E_{.1}$  was about 120 kJ/mol [Zhang *et al.*, 1994]. Without catalyst, the activation energy  $E_{.1}$  should be 367 kJ/mol, which is the carbon bond energy of graphite. That is the reason, without catalyst, diamond transforms into graphite at appreciable rates only at high temperatures (>2000K). However, graphitization occurs at relatively low temperatures (~970 K) when diamond is in contact with transition metals

with intermediate reactivity such as Fe, Ni, Co, Mn, and Cr, which can catalyse the conversion of diamond to graphite at low pressure and at temperatures above 700 °C [Butenko *et al.*, 2000, Ikawa, 1971, Sung, C. M. and Tai, 1997].

The surface temperature in polishing is discussed in Chapter 6. The lower limit of the surface temperature which is extrapolated from experimental measurement in the polishing conditions is over 740 °C. These high temperatures will stimulate the reactions between the polishing metal disk and diamond at the interface.

Whilst PCD is being polished, on the contact asperities of the PCD surface, the interface temperature rises above the critical point of the fast transformation of diamond due to the frictional heating. The contacting catalyst metals would accelerate the transformation, Thus diamond that is in contact with catalytic metal at these elevated temperatures loses its lattice structure and converts into non-diamond carbon. From the Raman analysis (detailed in Chapter 5), these non-diamond carbons ( $sp^2$  and  $sp^3$  bonding) were detected on the polished metal adhered surface and in the polishing debris, indicating that transformation had occurred during polishing. The results from HRTEM and EELS analysis have further confirmed the transformation of diamond to non-diamond carbons, which can be considered as the basic process of dynamic friction polishing. The non-diamond carbon is then removed mechanically as it was weakly bonded and/or by other chemical reactions.

However, in Iwai *et al.*'s PCD polishing experiments [Iwai *et al.*, 2001], the adhered films were removed by spraying SiO<sub>2</sub> on the disk and polishing was finished at lower pressure on the same machine after the dynamic friction polishing. The transformed non-diamond

carbon seemed to have been removed with the adhered film so that no trace of graphite was detected. Also in their XRD analysis, absence of graphite was probably due to the fact that the diffraction from non-crystalline graphite (or other carbon forms) was very weak, and the XRD could not detect it. Moreover, according to [Fedoseev *et al.*, 1986], surface graphitization of diamond is accelerated by oxygen-containing compounds in the gaseous phase. Thin graphite layers are formed on the surface of diamond, and then the graphite (not the diamond) is oxidized. Hence, during DFP under atmospheric conditions, surface graphitization of diamond and its oxidation is to be expected.

## 7.4 Oxidation of Carbon

When carbon (including diamond and graphite) is exposed to oxygen bearing environments at elevated temperatures, it would react with oxygen to form CO and/or CO<sub>2</sub> by the following reactions:



According to reaction kinetic theory, the reaction rate is

$$R_c = k_r (P_{O_2})^n (C)^n \quad (7.13)$$

$R_c$  is the rate of carbon (diamond) consumption (kg/s),  $P_{O_2}$  is the partial pressure of oxygen,  $C$  is concentration of carbon,  $n$  and  $k_r$  are reaction order and constant, respectively. Since

diamond is solid, the concentration of carbon can be taken as constant. The reaction rate can be written as

$$R_c = k (P_{O_2})^n \quad (7.14)$$

where  $k$  is the rate constant and obeys the Arrhenius equation:

$$k = A e^{-E/RT} \quad (7.15)$$

where  $T$  is absolute temperature,  $A$  is the pre-exponential factor of the Arrhenius equation,  $E$  is activation energy, and  $R$  is the gas constant.

According to equations 7.14 and 7.15, and Alam and Sun's experimental kinetic data [Alam and Sun, 1993], at a given oxygen pressure, the oxidation rate increases with increasing temperature. On the other hand, at a given temperature, diamond oxidizes faster with increasing oxygen partial pressure. Moreover, the oxidation rate also depends on activation energy which varies at different conditions. The apparent activation energy values which were determined by different research groups are presented in Table 7.1.

Table 7.1 Activation energies for oxidation of diamond published in literature

Source	Temperature range (K)	Other conditions	Activation energy (kJ/mol)
[Tankala <i>et al.</i> , 1990]	873-1073	Air, atmospheric pressure, 0.5 L/min	151
[Johnson <i>et al.</i> , 1990b]	873-1023	Air, atmospheric pressure, no flow. Increasing humidity inhibit oxidation, CVD film	213
[Alam and Sun, 1993]	973-1073	25-100 vol.% O <sub>2</sub> (balance Ar), 1 atm pressure, 1 L/min. HF-CVD polycrystalline	232
[Sun and Alam, 1992]	973-1173	Pure O <sub>2</sub> , atm. Pressure, 1 L/min	260
		Natural (111)	199
		Natural (100)	229
		CVD polycrystalline	229

The discrepancy among the activation energy values may be attributed to differences in the diamond structure, particularly in terms of film morphology, crystallite size, amount of non-diamond carbon, hydrogen, etc. and crystal defects [Alam and Sun, 1993].

It has been shown that non-diamond carbon oxidizes more rapidly than diamond [Alam and Sun, 1993, Joshi *et al.*, 1990]. Also  $sp^2$  bonded carbon is generally known to oxidize faster than  $sp^3$  bonded carbon [Joshi *et al.*, 1990]. The activation energy for graphite varies from 155 to 184 kJ/mol [Johnson *et al.*, 1990a, Joshi *et al.*, 1990], while that for a diamond film is from 213 to 240 kJ/mol [Alam and Sun, 1993, Johnson *et al.*, 1990a, Nimmagadda *et al.*, 1990].

In addition, the oxidation of carbon can be accelerated by catalysts in a number of ways. Some research found out that elements that catalyse carbon-oxygen reactions include Na, K, Ca, Cu, Ti, Fe, Mo, Cr, Co, Ni and V [Luo *et al.*, 2004]. The heterogeneous distribution of impurity leads to the dispersibility of oxidation results. Inui [Inui *et al.*, 1982] ranked the oxidation activities of single metal component catalysts at temperature about 500°C at atmospheric pressure as Cu>Co>Fe>Ni>Pt. Many investigations show that the metals or metal oxides of Pb, Co, V, Mo, Fe, La, Mn, Ca, Cu, Ni and Cr are very active to moderately active carbon oxidation catalysts [Mul *et al.*, 1998, Neeft *et al.*, 1997]. The nature of catalysis involves either activation of carbon atoms or acting as a source of activated oxygen. During the oxidation of carbon, the catalyst metal also get oxidized and reduced. Before the catalyst metal is completely oxidized, oxygen is rapidly transferred

onto carbon to form CO<sub>2</sub>. On the other hand, the oxidation rate of the metal is faster than the reduction rate of metal oxide by active carbon at 500°C.

Inui *et al.* also found out that the activity of the two or three component catalyst system was greater than the sum of the activities of each catalyst system taken separately [Inui *et al.*, 1982]. This synergistic effect was observed in Fe-La<sub>2</sub>O<sub>3</sub>-Pt, Fe-Mn<sub>2</sub>O<sub>3</sub>-Cu catalyst or when Co or Ni was used as the main component of the catalyst. The rate enhancement of carbon-oxidation in the composite catalyst system can be explained as: oxygen in the gas phase is rapidly taken up by one kind of metal particle; this adsorbed oxygen is easily transferred successively to the carbon via another partially reduced metal oxide. Since two different roles of each catalyst were combined in the composite catalyst, consequently, the oxidation reaction must be promoted with the synergistic effect [Inui *et al.*, 1982].

As can be seen, metals or metal oxides of Co, Mo, Fe, Mn, Cu, Ni and Cr are active carbon oxidation catalysts, and the combination of metal or metal oxide will notably increase the carbon oxidation rate.

According to [Alam and Sun, 1993, Tankala *et al.*, 1990], neither x-ray diffraction nor Raman spectroscopy data revealed any phase transformation of diamond to either crystalline or amorphous non-diamond carbon phases after oxidation in air or oxygen gas. The oxidation behaviour of diamond is consistent with two reaction paths [Tankala *et al.*, 1990]. (i) Diamond can oxidize directly to CO and CO<sub>2</sub>. (ii) If diamond is to oxidize via an intermediate product such as graphite, as has been reported to occur under certain oxidation

conditions for natural diamond, the oxidation of the intermediate product occurs at a rate which is not slower than its rate of formation.

Natural diamond is stable in inert environments up to temperatures of 1300-1500 °C and above this temperature it will transform to graphite [Johnston *et al.*, 1992]. In oxidizing atmospheres diamond is decomposed at temperatures as low as 700-800 °C via oxidation to gaseous products which are presumably CO or CO<sub>2</sub> or a mixture of them. At low oxygen pressures the diamond surface may contain graphite which is also converted to gaseous products at lower activation energy in this temperature regime. Diamond is reasonably stable in flowing oxygen at temperatures up to 600 °C. Above 600 °C oxidation of the diamond films has been observed to take place at a measurable rate. The oxidation rate increases with further temperature increases until at temperatures greater than 800 °C diamond only survives momentarily.

In the present experiments, PCD is polished under atmospheric conditions, and the lower limit of the surface temperature rises above 740 °C (section 7.3). Hence, the diamond or transformed non-diamond carbon, exposed to oxygen, would react with oxygen to form CO and/or CO<sub>2</sub> gas. According to the Raman spectroscopy analysis (section 5.5.3 and 5.6.3, Chapter 5), there was no indication of presence of graphite from the polishing debris and the graphite band could hardly be detected in the metal/oxide adhered specimen, while the *sp*<sup>3</sup> bonded carbon could be detected in the adhered specimen and polishing debris, and the intensity of the graphite band became stronger in the metal/oxide removed PCD specimen. The reason is that graphite, which was converted from diamond, had oxidized in the oxygen environment and escaped as CO or/and CO<sub>2</sub> gas, or partly remained in the PCD

specimen covered by the adhering film. After the metal/oxide film was removed, a thin graphite layer could be found on the PCD specimen. Since the non-diamond carbons oxidize more rapidly than diamond, and  $sp^2$  bonded carbon faster than  $sp^3$  bonded carbon, after the transformation of diamond ( $sp^3$  bonded) to non-diamond carbon ( $sp^2$  and  $sp^3$  bonded) has occurred,  $sp^2$  bonded carbon would be oxidized quickly, while  $sp^3$  bonded carbon still remains on the polished metal/oxide adhered surface and polishing debris. Also in Suzuki *et al.*'s experiments [Suzuki *et al.*, 2003], there was a marked increase in the material removal rate in the oxygen atmosphere, supporting oxidation in an oxygen environment.

## 7.5 Diffusion of Carbon into the Metal Disk

Carbon atoms easily diffuse into high carbon soluble metals. These metals include rare earth alloys and, Fe, Ni and Mo. They have a chemical characteristic known as carbon solubility potential, they are ready to react with any source of free carbon and absorb this carbon into their surface. The carbon concentration of a metal in contact with a carbon source is given by [Malshe *et al.*, 1999]:

$$C(y) = C_1[\operatorname{erfc}(y/2\sqrt{Dt})] \quad (7.16)$$

where  $C(y)$  is the carbon concentration at  $y$ ,  $C_1$  is the interface carbon concentration,  $\operatorname{erfc}$  is the error function,  $y$  is the distance from the interface,  $D$  is the diffusion coefficient, and  $t$  is time.

One of the metal disk elements, iron, possesses one of the highest diffusion coefficients for carbon among the group VIII B transition metals [Zaitsev *et al.*, 1998], though its value drops with increasing carbon concentration. Iron also has a high solubility of carbon reaching  $170 \text{ mg/cm}^3$  at the eutectic temperature. In the polishing disk material, the initial carbon concentration is lower than 0.08%, and the disk is very big (450 mm diameter) and thick (section 4.3.2, Chapter 4) compared to the PCD specimen (12.7 mm diameter). Moreover, the disk material SUS304 is in austenite structure, and the maximum carbon solubility in austenite is as high as 2.03% C at  $1147 \text{ }^\circ\text{C}$  [2004]. Therefore, such diffusion reaction is easily triggered under the temperature and pressure conditions occurring in the dynamic friction polishing process.

When a diamond surface comes into contact with a metal disk at high temperatures, converted carbon atoms in diamond diffuse into the metal disk until the metal is saturated. The diffusion path for atoms from protruding parts of the specimen is shorter and these areas are attacked at a greater rate, and the diffusion rate of graphite is much greater than that of diamond [Vishnevskii *et al.*, 1975]. In Iwai *et al.*'s [Iwai *et al.*, 2001] EDX analysis, carbon was detected in the polishing metal disk and the adhered film, while in Suzuki *et al.*'s [Suzuki *et al.*, 2003] XRD analysis of the disk surface after polishing, a carbonization trace ( $\text{Fe}_3\text{C}$ , cementite) was detected, and EPMA analysis indicated that there was an increase in the carbon element content in the surface in contact with the diamond. When iron and carbon combined forming Fe- $\text{Fe}_3\text{C}$ , the carbon concentration could reach to 6.67%C. These results indicate that there was diffusion of carbon into the metal disk surface. One of the factors involved in diamond polishing is considered to be the diffusion

of carbon into the metal disk and form iron austenite after the transformation of diamond to non-diamond carbon.

However, the actual rates of carbon diffusion are strongly determined by the PCD-metal interface conditions [Zaitsev *et al.*, 1998]. The diffusion is an atomic process, and requires a good physical PCD-metal contact literally for every diffusing atom. In addition, Weima *et al.* [2001] found that the removal rate dropped exponentially with increasing speed of the polishing plate during thermo-chemical polishing [Weima *et al.*, 2001]. This drop was attributed to the reduction in the surface contact between the diamond film and the polishing plate. In the present dynamic friction polishing, the polishing speed is much higher than that in thermo-chemical polishing, thus the diffusion rate would not be very high. Therefore the diffusion of carbon to metal disk can only be considered as part of the removal mechanism instead of dominating the removal mechanism as proposed by Suzuki *et al.* [Suzuki *et al.*, 2003].

## **7.6 Summary of Polishing Mechanism**

From the model developed in Chapter 6 to predict the temperature rise in dynamic friction polishing, the PCD-metal interface temperature was estimated to be above 1150K. The elevated temperature would stimulate the reactions between the polishing metal disk and diamond at the interface. In addition, the contacting catalyst metals would accelerate the transformation of diamond to non-diamond carbon. The results from Raman, HRTEM and

EELS analyses discussed in Chapter 5 have confirmed the existence of these non-diamond carbons ( $sp^2$  and  $sp^3$  bonding) and hence the transformation of diamond to non-diamond carbons, which can be considered as the basic process of the dynamic friction polishing. Meanwhile, another component of PCD, SiC, also chemically reacted and was transformed to amorphous silicon oxide/carbide during the polishing condition, as detailed in section 5.6.4.

After the transformation occurs, the surface of the contact asperities becomes much softer, and it is easily removed with the adhered metal/oxide due to the motion between the disk and PCD surface. SEM and EDX analyses in Section 5.6.1 indicated that carbon was removed with catalyst metals/oxide in particle-like debris. In addition, Raman spectroscopy, HRTEM and EELS analyses discussed in sections 5.6.3 and 5.6.4 have confirmed that the non-diamond carbon and amorphous silicon oxide/carbide were removed in polishing debris.

Additionally, on the contact asperities, diamond and its transformed non-diamond carbon were exposed to oxygen at high temperatures. They could easily react with oxygen and escape as CO and/or CO<sub>2</sub> gas. In addition, the oxidation of carbon would be accelerated by the catalyst metals or metal oxides of Fe, Ni and Cr from the polishing disk. Moreover, diffusion of the carbon from PCD to metal disk is another process contributing to the material removal.

The basic polishing process involves the interaction of diamond with the rotating metal disk and conversion of diamond into non-diamond carbon, and SiC to amorphous silicon

oxide/carbide. After the transformed layer and adhered film were removed, new asperities would contact with the metal disk, and the transformation and removal of the adhered film are repeated by rotation of the disk, and the PCD material (diamond and SiC) will be continuously removed. This process results in a polished PCD surface.

Figure 7.3 summarizes the material removal mechanisms and the associated chemical reactions in the dynamic friction polishing process.

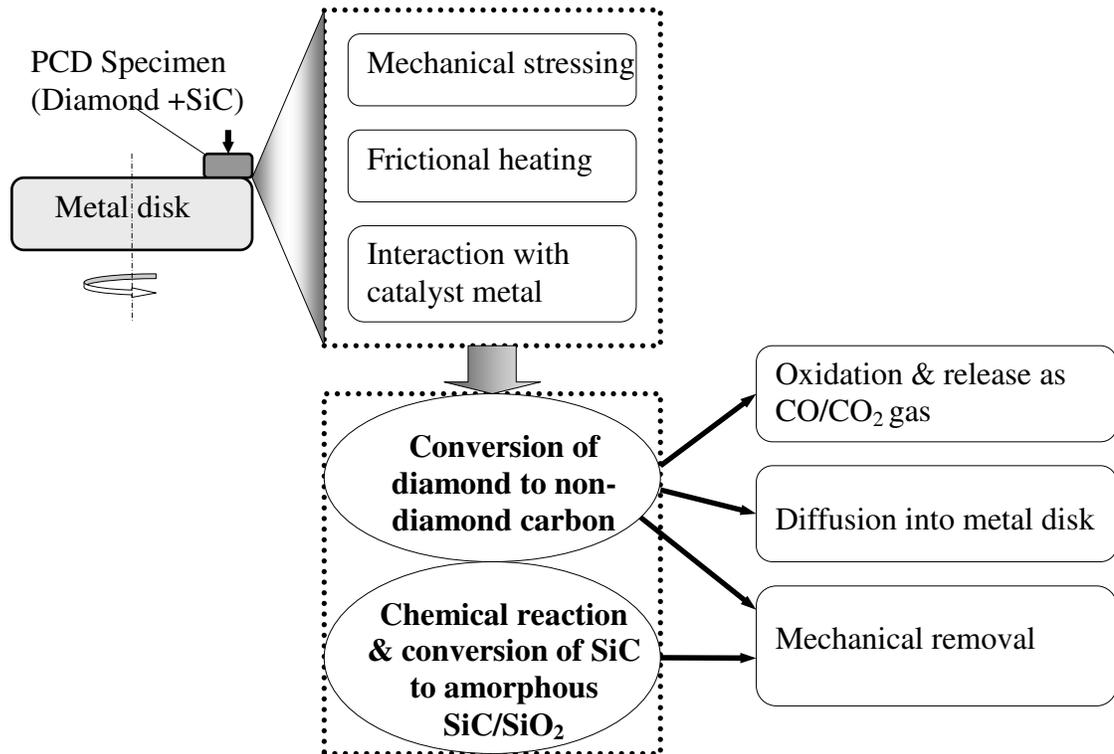


Fig.7.3 The mechanism map of material removal in dynamic friction polishing

In conclusion, based on the experimental results and theoretical analyses, the material removal mechanism of dynamic friction polishing can be described as follows: conversion of diamond into non-diamond carbon takes place due to the frictional heating and the interaction of diamond with the catalyst metal disk; then a part of the transformed material is detached from the PCD surface as it is weakly bonded; another part of the non-diamond carbon oxidizes and escapes as CO or CO<sub>2</sub> gas and the rest diffuses into the metal disk. Meanwhile, another component of PCD, SiC also chemically reacts and transforms to amorphous silicon oxide/carbide, which is then mechanically/chemically removed.