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The Effects of MAPCVD-Diamond Coating on the Phase Stability and Microstructure of Zirconia (Y-TZP) Cutting Tool Inserts

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ABSTRACT

Yttria-tetragonal zirconia ceramics (Y-TZP) ceramics is considered as one of the most promising material for cutting tool applications due to its unique combination of chemical, physical and mechanical properties. Although Y-TZP ceramics is tough and strong, tool bits need to be simultaneously hard, tough and wear resistant. However, high hardness is usually associated with brittleness. Hence, there always has to be a compromise between the desired hardness and the necessary toughness. In the present work, the effect of coating a thin film of diamond on the surface of Y-TZP inserts by employing Microwave Plasma Chemical Vapour Deposition (MAPCVD) technique was studied. The Y-TZP inserts were prepared and sintered to full density at 1400°C prior to MAPCVD process. Selected sintered inserts were surface-ground using a coarse and fine SiC paper while another was polished to 1 μm finish prior to MAPCVD treatment. It has been found that nucleation of CVD diamond particles only occurred on Y-TZP surface polished to 1 μm finish. X-ray diffraction (XRD) analysis performed on other Y-TZP inserts did not revealed any strong peaks corresponding to crystalline diamond phase and these were confirmed using scanning electron microscopy (SEM). However, chemical reaction between Zr and carbon from the reducing atmosphere in the chamber did occur in all of the treated inserts to form a new phase, ZrC. Although diamond nucleation was not observed in both the pre-ground and CVD treated surfaces, SEM examination of these so treated surfaces revealed fine-grained structure believed to have recrystallised from the severely damaged ground surface.

Keywords: Zirconia ceramics, Y-TZP, MAPCVD, diamond coating, cutting tool inserts, recrystallisation

INTRODUCTION

Diamond is the hardest material known to exist. It is accessible in both, single crystal and polycrystalline form. In general, diamond is an exceptional material for countless applications, due to the unique combination of physical and chemical properties.

Some of these properties include highest thermal conductivity, lowest thermal expansion coefficient, highest molar density, highest hardness and lowest compressibility (May 1995). In addition, with the invention of synthetic growth techniques at high pressure and temperatures (Stinton *et al.* 1988), today, diamond became a technical material, especially for mechanical applications (Itoh *et al.* 1997).

In contrast, yttria-tetragonal zirconia polycrystalline ceramics (Y-TZP) is one of the most promising material for structural applications due to its excellent wear resistance, high strength (> 1500 MPa) and high toughness (> 5 $Mpam^{1/2}$) (Birkby and Hodgson 1993; Ramesh *et al.* 1996). This improved mechanical properties of Y-TZP ceramics are attributed mainly to a phenomenon known as transformation toughening (Garvie *et al.* 1975).

In this mechanism, the tetragonal particles (t) in the zirconia matrix would absorb energy from an external stress (e.g. a passing crack) and transform to the monoclinic (m) polymorph with an associated volume expansion of ~ 3.5%. This, in turn, would

suppress crack propagation by exerting compressive stresses against the advancing crack. Thus, Y-TZP ceramics has been employed in many structural applications including cutting tools (Annamalai *et al.* 1991; Sornakumar *et al.* 1993).

During machining, cutting tools are usually subjected to pressure and temperature. Under such hostile environment, tool wears or fails by any one of the following mechanisms such as edge chipping, thermal cracking, adhesion, abrasive wear, plastic deformation, oxidation, etc. (Annamalai *et al.* 1991; Lo Casto *et al.* 1996).

For this reason, tool materials should possess improved physical, chemical and mechanical properties at elevated temperatures. Although, Y-TZP ceramics is tough and strong, tool bits need to be simultaneously hard, tough and wear resistant. However, high hardness is usually associated with brittleness. Hence, there always has to be a compromise between the desired hardness and the necessary toughness.

Therefore, in order to take advantage of the extreme high hardness of diamond and the transformation toughening of zirconia, a study on the possibility of nucleating CVD diamond particles on the surface of Y-TZP inserts using MAPCVD technique was undertaken.

Studies on the synthesised diamond particles using MAPCVD methodologies have received substantial consideration due to the many potential applications of diamond films in various industries (Sherman 1984; Saito *et al.* 1986; Lin *et al.* 1992; Inderjeet *et al.* 1998). However, for actual application of diamond coating to non-diamond surfaces, improvement of 2 adherence between diamond film and substrate is one of the most important problems to be solved (Stinton *et al.* 1988).

The main reason for the low adherence strength is due to large difference in the thermal expansion coefficient between diamond and sample material resulting in thermal stresses being generated during the cooling process. Although concerted effort have been devoted in solving this problem e.g. surface pretreatment, etc., adherence is still insufficient for reliable application to cutting tools. In particular, very little data is available on the CVD diamond coating of zirconia inserts.

The objectives of the present work are : (i) to employ MAPCVD technique to nucleate diamond particles on the surface of 3 mol% Y-TZP ceramics insert; (ii) to study the effects of surface pretreatment such as grinding and polishing of Y-TZP surface on the nucleation of diamond particles; (iii) to study the effect of MAPCVD treatment on the phase changes and microstructure evolution of Y-TZP ceramics.

MATERIALS AND METHODS

The as-received commercially available Y-TZP powder containing 3 mol% yttria (Kyoritsu Co. Ltd. Japan) was used in this study. The inserts were made by pressing the powder into cylindrical shape in a 20 mm die followed by cold isostatic pressing at 200 MPa. The green inserts were sintered at 1400°C, at a furnace ramp rate of 10°C/min. and holding time of 2 hours in order to restrict grain growth.

Deposition of the diamond particles was conducted in a custom built microwave plasma chamber using methane and hydrogen as the feed gases. The system layout is as illustrated in Figure 1. The parameters of the gas composition, pressure and microwave power were set accordingly to create a plasma ball which eventually will heat up the insert and consequently deposits diamond crystals on the surface.

Characterisation and Properties Evaluation

The relative density of the ceramic inserts was determined by water immersion method. Phase analysis by X-ray diffraction (XRD) of inserts was carried out at room temperature

using Cu-Kα as the radiation source. The crystalline phases present in the samples were identified by comparing with reference to standard JCPDS files available in the system. Fraction of the tetragonal and monoclinic phase retained in the zirconia after sintering was determined using the method of Toraya *et al.* (1984). Fracture toughness and hardness were measured using the Vicker's indentation method (Niihara *et al.* 1982).

In addition, microstructural evolution of the composites was examined by scanning electron microscopy (SEM) and grain size was determined from the scanning electron micrographs (Mendelson 1969).

In the present work, four zirconia inserts were prepared and tested as designated in Table 1. These inserts were as-received, ground to introduce rough and fine scratches using SiC paper while another was ground and polished to 1 μm surface finish. The prepared inserts were then cleaned ultrasonically in acetone and water. The inserts were then dried in air prior to mounting them in the stainless steel chamber, see (Figure 1). The CVD process was carried out at ~ 1000°C for 6h.

TABLE 1
The starting Y-TZP Inserts prior to coating

Insert no.	Surface condition
Z1	As-received
Z2	Surface ground using coarse (120 grit) SiC paper
Z3	Surface ground using fine (1200 grit) SiC paper
Z4	Surface ground & polished to 1 μm surface finish

After the treatment, the presence of diamond phase carbon on the deposited surface was verified at room temperature by X-ray diffraction. The distribution of the deposited particles on the insert surface and the morphology of the diamond particles were studied by using the scanning electron microscopy.

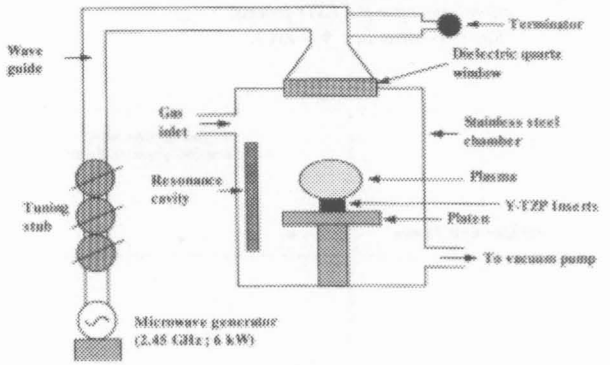

Fig. 1. A schematic diagram showing the layout of the microwave plasma reactor used in the present study.

RESULTS & DISCUSSION

Mechanical Properties

The starting properties of the as-received zirconia inserts are summarised in Table 2.

TABLE 2
Average properties of the starting Y-TZP inserts

(t) (%)	ρ (Mgm^{-3})	H_v (GPa)	K_{Ic} ($MPam^{1/2}$)	(t) grain Size (μm)
100	6.04	12.5	~ 5	0.3

In general, it has been found that the inserts composed of (t) structure, high bulk density ≥ 6 Mgm^{-3}, fine grain size, high toughness and moderate hardness.

X-Ray Diffraction (XRD) Analysis

The XRD patterns of the inserts before and after the CVD process are presented in Figures 2 - 5.

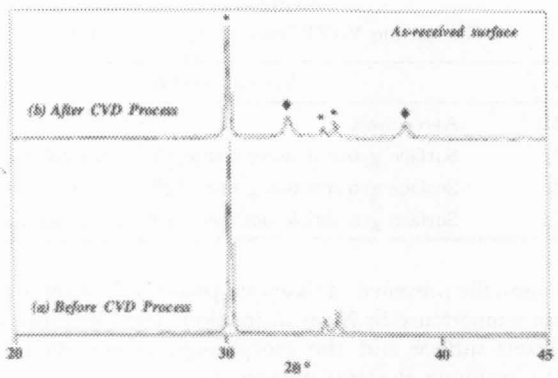

Fig. 2. XRD patterns of the insert Z1 showing the phases present before and after the CVD process. (Key : • - zirconia ; ♦ - ZrC).

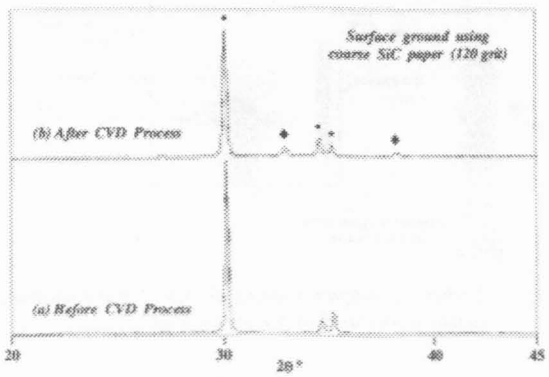

Fig. 3. XRD patterns of insert Z2 after the CVD process. (Key : • - zirconia ; ♦ - ZrC).

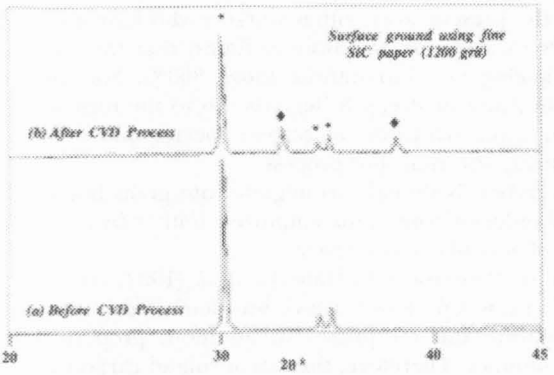

Fig. 4. XRD patterns of insert Z3 after the CVD process (Key : • - zirconia ; ♦ - ZrC).

The general observations that can be drawn from the four XRD patterns are :

i. During the CVD process, a chemical reaction between the C from the atmosphere and Zr had taken place to form zirconium carbide (ZrC).

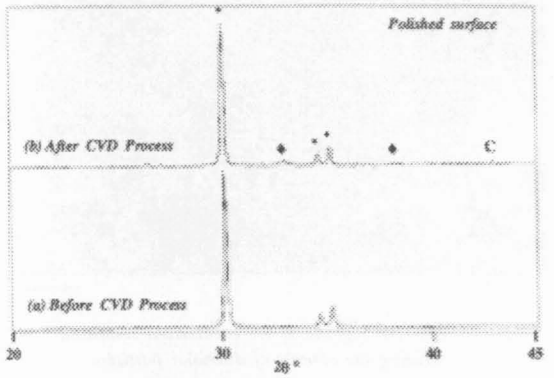

Fig. 5. XRD patterns of insert Z4 after the CVD process. Note the presence of diamond phase carbon. (Key : • - zirconia ; ♦ - ZrC).

ii. No monoclinic phase was detected in any of the insert after the CVD process indicating that the tetragonal phase was stable under the employed deposition conditions.
iii. The nucleation of CVD diamond particles was not detected on the as-received surface (Figure 2), on the rough abraded surface (Figure 3) and also on the fine abraded surface (Figure 4).
iv. The presence of some diamond phase carbon was only detected on the surface which was ground and polished to 1 μm finish (Figure 5).

At this stage, it is still unclear of the formation of ZrC and how does this phase effect the properties and performance of the zirconia inserts.

In relation to the present work, other workers who have studied the effects of hot-pressing of Y-TZPs in reducing atmosphere found that the strength of the ceramics deteriorate after ageing at temperatures above 800°C. For instance, Masaki (1986) attributed the main cause of strength degradation to the formation of grain boundary cavitation resulting from oxidation of carbon species that were incorporated in the zirconia matrix during the sintering process.

This remnant carbon is thought to migrate into grain boundaries of the zirconias due to the highly reduced conditions employed (either in N_2 or Ar gas atmosphere) within a graphite element-heated furnace.

In contrast, in another research, Haberko *et al.* (1992) reported that small amount of carbon (~ 0.17 wt% was detected) which was deposited in the zirconia structure was beneficial in stabilising the (t) phase. In addition, property degradation was not observed in these samples. Therefore, the actual role of carbon in the ZrO_2 structure is still unclear.

Scanning Electron Microscopy (SEM)

In order to confirm the presence of CVD diamond-like carbon on the treated surface, scanning electron microscopy was employed, see Figures 6-9.

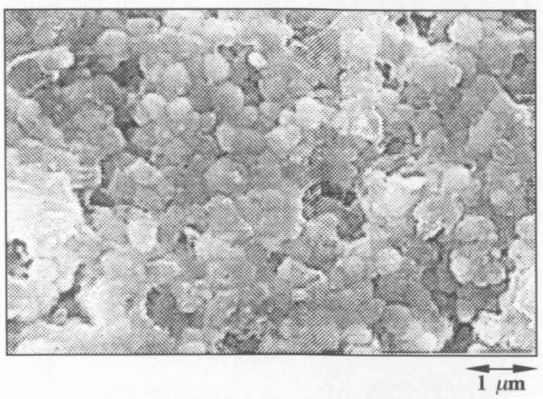

Fig. 6. SEM micrograph of Z1 (as-received condition), showing the absence of diamond particles

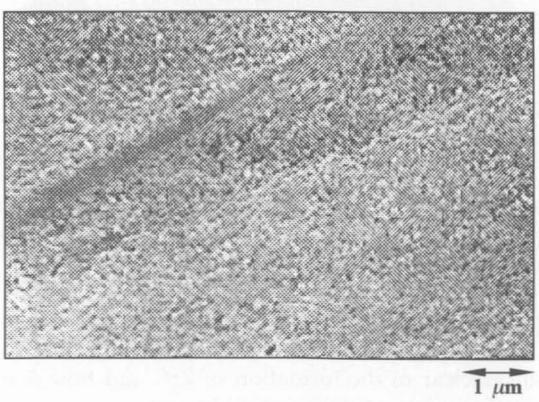

Fig. 7. SEM micrograph of Z2 (rough abraded surface). No diamond particles were observed. Note the very fine-grained surface region which was not observed in Z1.

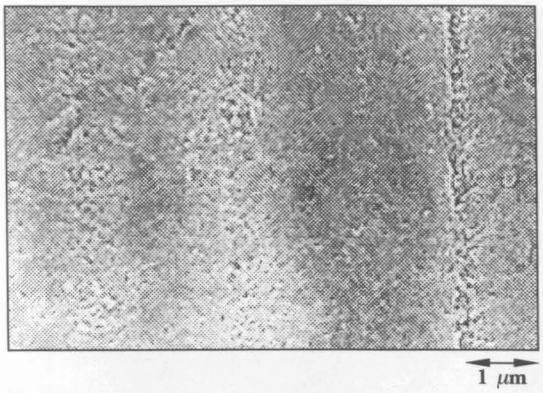

Fig. 8. SEM micrograph of Z3 (finely ground surface), indicating no sign of diamond particles on the surface. The fine-grained structure observed in Figures 7 and 8 is believed to have resulted from surface recrystallisation caused by grinding and the MAPCVD treatment.

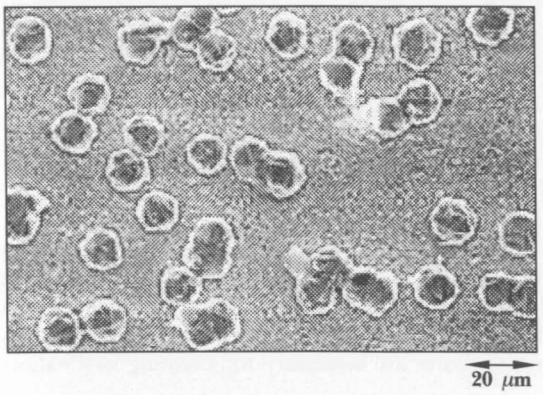

Fig. 9. Nucleation of CVD diamond like carbon particles on the polished surface (Z4 insert).

The SEM analysis of Z1, Z2 and Z3 did not show the presence of CVD diamond on the surface (see Figures 6 to 8) and is in good agreement with the XRD analysis. However, only sample Z4 which was polished to 1 μm finish exhibited nucleation activity of CVD diamonds on the surface (see Figures 9 and 10).

Based on the evidence provided by the SEM analysis, the following observation can be drawn :

i. The scratch marks (rough and fine) which were deliberately introduced on the surface of Y-TZP insert prior to MAPCVD treatment did not provide the avenue for CVD diamond nucleation.
ii. On the other hand, polishing the Y-TZP surface to mirror finish i.e. to 1 μm (Sample Z4) was found to be effective in aiding nucleation of diamond particles. Several studies have shown that pre-abrasion of non-diamond surfaces was beneficial in reducing the induction time for nucleation and increases the density of nucleation sites. This, in turn, would enhance growth rates since the formation of a continuous

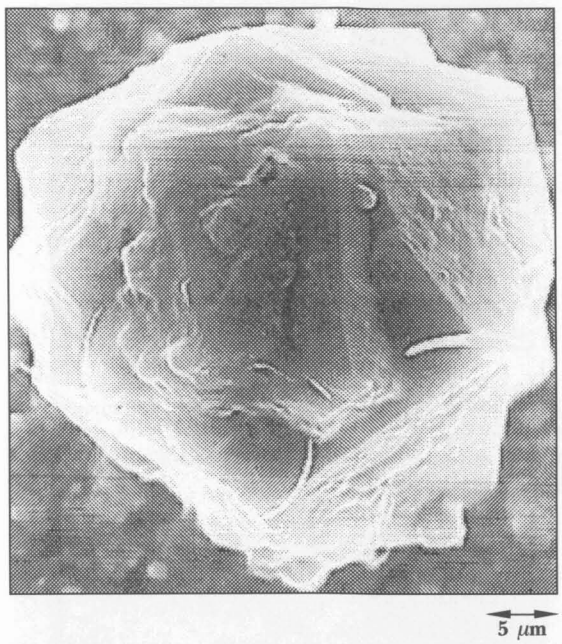

Fig. 10. Close-up view showing the morphology of the deposited CVD diamond particle on Z4 surface. The average size of the diamond particle is ~ 13.5 μm.

diamond film is a process of crystallisation, proceeding via nucleation, followed by three-dimensional growth of the various microcrystallites to the point where they eventually coalesce into a continuous film. Therefore, in the present work, it can be inferred that for Y-TZP materials submicron scratches such as those introduced during polishing to 1 μm are necessary for creating nucleation sites for diamond particles.

iii. In general, it can be observed that a homogeneous distribution of diamond particles of uniform sizes was nucleated on the polished surface. The average size of the diamond particles was ~ 13.5 μm.

iv. However, a poor nucleation density (determined to be ~ 2.1 x 10 5 cm^{-2}) with not well formed diamond particulate was observed on the polished surface. As illustrated in Figure 10, the particle lacks the faceted features of a diamond crystal. It should be mentioned here that only a deposition time of 6 hours was used throughout this experiment, so the deposition time needed for optimum diamond nucleation and formation was not assessed.

v. The poor nucleation density of CVD diamond on the surface of Y-TZP ceramics could in part be attributed to the large difference in thermalexpansion coefficient between both materials (see Table 3). Therefore, residue stresses would be generated at the interface and this would inevitably leads to poor adhesion.

vi. It has been found that surface recrystallisation had occurred on the Y-TZP surface abraded using the coarse and fine SiC paper and exposed for 6 h at 1000ƒC in the MAPCVD chamber. XRD and SEM analysis indicated that there were no CVD diamond deposited on these abraded surfaces (i.e. insert Z2 and Z3). However, the SEM analysis of these surfaces revealed very fine-grained structure which is believed

TABLE 3
Thermal expansion coefficients of materials

Thermal expansion coefficient (x 10^{-6} °C)		
	Diamond	Zirconia
at room temperature	0.8	8
at 1000°C	2.6	10

to have recrystallised on the damaged surface. This is clearly illustrated in Figures 6, 7 and 8. All these SEM pictures were taken at the same magnification. The average grain sizes determined on the insert surfaces after exposure for 6 h at 1000°C in the MAPCVD chamber are presented in Table 4.

TABLE 4
Average grain size of ground/exposed Y-TZP surfaces

Surface condition	Grain size (μm)
As-received	0.3 – 0.35
Ground using coarse (120 grit) SiC paper	0.09 – 0.1
Ground using fine (1200 grit) SiC paper	~ 0.1
Polished to 1 μm surface finish	~ 0.3

vii. However, no sign of recrystallisation was observed on the Y-TZP surface polished to 1 μm finish. These results correlate well with the work of Whalen, *et al.* (1989). These authors investigated the effects of grinding and annealing on the degree of recrystallisation in Y-TZP ceramics. The annealing was carried out for 2 hours in air and at temperatures ranging from 900°C to 1500°C. A significant difference in grain size was noted between the bulk and abraded/recrystallised region, except for the 1500°C annealed sample.

viii. Recrystallisation phenomenon is well established in metallurgy but is not common in oxide ceramics. In general, for recrystallisation to occur, sufficient strain energy must be stored in the material so that, on heating, new-strain free grains can nucleate and grow. In the present work, stresses were generated in the ground/exposed surface. This was indicated by comparing the XRD peak under the (111) region of the tetragonal phase which showed that peak broadening only occurred in the ground/exposed surface. Peak broadening was not observed in the as-received/exposed and polished/exposed surface. Therefore, based on these results, it is envisage that the plastic deformation couple with general surface damage induced during grinding is essential for successful recrystallisation. The contribution of additional stresses arising from the CVD process due to the large difference in thermal expansion coefficient between diamond and Y-TZP materials, would have further facilitated recrystallisation in these abraded surfaces. Further work is in progress to elucidate this phenomenon.

CONCLUSIONS

The effects of CVD diamond coating using MAPCVD technique on the phase stability and microstructure of Y-TZP inserts which have been ground and polished were studied. XRD analysis revealed that reaction between Zr and C did occur in all the insert tested.

The introduction of macro scratches during surface grinding of Y-TZPs did not provide the necessary conditions for nucleation of diamond particles. However, Y-TZP surface polished to mirror finish (~ 1 μm finish) facilitated the nucleation of diamond particles. Submicron scratches appear to be one of the essential conditions for the success of diamond nucleation on Y-TZP surfaces. The surface region of Y-TZPs can be recrystallised into fine-grained structure through the use of grinding to introduce macro-scratches and MAPCVD treatment at ~ 1000°C.

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NOTATION

ρ	Bulk Density
CVD	Chemical Vapour Deposition
C	Carbon
K_{Ic}	Fracture Toughness
(t)	Tetragonal ZrO2
H_v	Vickers Hardness
Y-TZP	Yttria-Tetragonal Zirconia Polycrystal
ZrO_2	Zirconia

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