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Development of Zirconia Nanocomposite Ceramic Tool and Die Material Based on Tribological Design

Chonghai Xu[1,2], Mingdong Yi[2], Jingjie Zhang[1],
Bin Fang[1] and Gaofeng Wei[1]
[1]Shandong Polytechnic University
[2]Shandong University
PR China

1. Introduction

With the development of modern manufacturing technology, die is more and more need in high temperature, high pressure, special working conditions or complex working condition [Liu & Zhou, 2003]. The requirement in mechanical properties of die material becomes higher and higher. It is necessary to improve the new die material [Kar et al, 2004]. Structure ceramics, because of its high hardness, high temperature mechanical property, wear resistance and corrosion resistance, have been widely used [Basu et al, 2004]. However, lower fracture toughness has limited its wide applications. Moreover, the tribological characteristics also need further study [Hirvonen et al, 2006].

Tetragonal zirconia polycrystal (TZP), with lower sintering temperature and high sintering density, have got wide application in modern die industry because of the excellent mechanical properties and transformation toughening effect[Guicciardi et al, 2006]. However, the low hardness restricts their tribological applications [Zhang et al, 2009; Liu & Xue, 1996; Yang & Wei, 2000]. Titanium diboride (TiB_2) has an excellent hardness and wear resistance but with poor fracture toughness and flexural strength [Baharvandi et al, 2006]. The proper addition of TiB_2 can improve the hardness of ZrO_2 nano-composite ceramic tool and die material with the other mechanical properties still not being decreased [Basu et al, 2005].

The excellent mechanical properties of TZP ceramics are decided mainly by the transformation toughening [Hirvonen et al, 2006]. Stabilizer materials should be added into the zirconia ceramic to obtain the tetragonal zirconia at room temperature for the achievement of the transformation toughening effect [Gupta et al, 1977]. Yttria is one of the most popularly used stabilizers. The incorporation of Y_2O_3 can lower the sintering temperature and enhance the sintering density, so that both mechanical properties and wear resistance can be improved. However, the excessive addition of Y_2O_3 will cause the difficulty of the tetragonal zirconia to be transformed into the monocline one, reducing the transformation toughening effect.

Sintering is also the key process in the preparation of ceramic materials to achieve material with high performance of the composite material with defined raw materials [Hannink et al, 2000]. Nanometer grain which has high surface energy and activity can grow fast and move quickly in the sintering process. Using hot pressing technology can lower the sintering temperature and shorten the holding time. The sintering temperature and the holding time are the key sintering parameters to achieve high performance of nano-composite material [Guicciardi et al, 2006]. Moreover, the sintering parameters play an important role on the improvement of mechanical properties through the increase in the transformation toughening effect [Tu & Li, 1997].

From the friction and wear problems in the application of the existing ceramic tool and die materials, it is necessary to carry out tribological design during the material research. In the present study, a new nanocomposite ceramic tool and die material was prepared by vacuum hot pressing technique with the application of the tribological design, and the processing techniques, microstructure, mechanical properties and the friction and wear behavior was studied.

2. Experiments

ZrO_2 stabilized by 5mol% Y_2O_3(5Y-ZrO_2), TiB_2 and Al_2O_3 are the main raw materials with the average particle size of 40nm, 1.5µm and 1.5µm, respectively. Both 5Y-ZrO_2 and TiB_2 are all commercial powders. The Al_2O_3 powders were obtained by roasting the analytically pure $Al(OH)_3$ powders. Before the experiment, TiB_2 and Al_2O_3 powders were ball milled for 100 hours.

As shown in Fig. 1(a), the particle size of commercial TiB_2 powder is about 10µm, while that after ball milling is only about 1.5µm (Fig. 1(b)).

Fig. 2 and Fig. 3 are the results of X-ray energy dispersive analysis and particle size analysis, respectively. As shown in Fig. 2, the Al_2O_3 powders have nothing impurities. The average particle size of Al_2O_3 is about 1.5µm (Fig. 3).
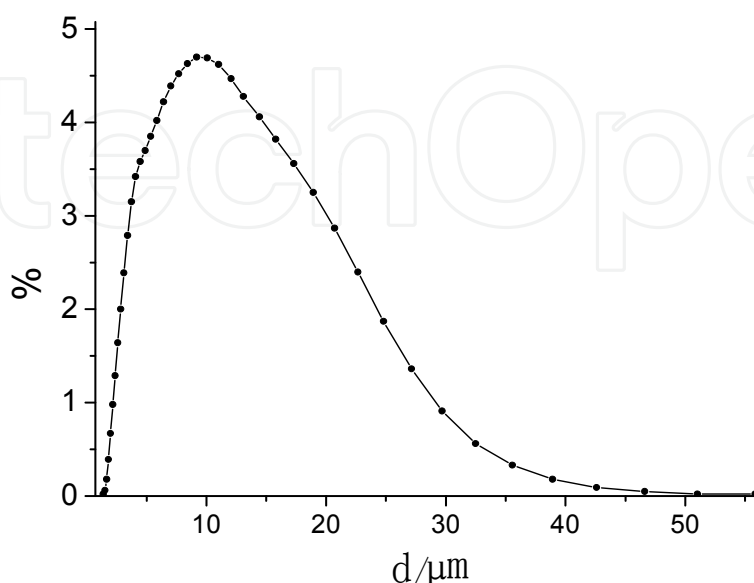
(a) commercial powders
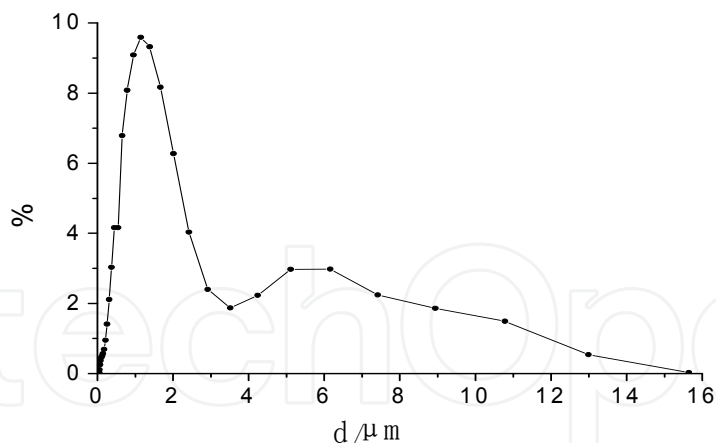
(b) after ball milling

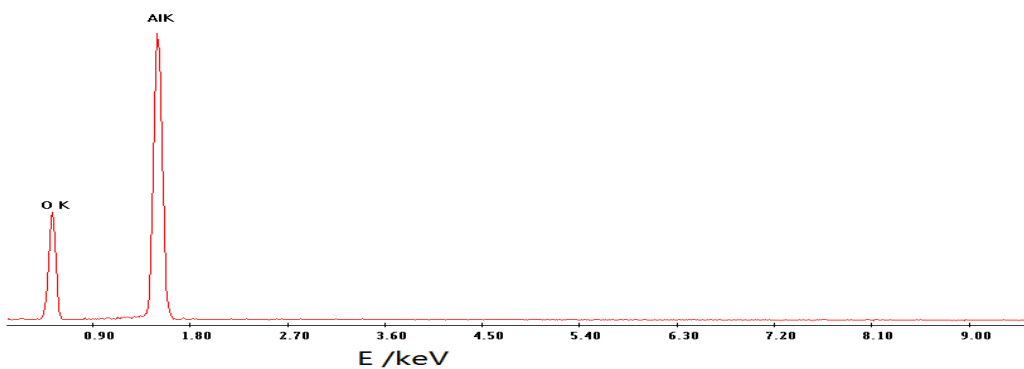Fig. 1. Particle size distributions of TiB$_2$ powder
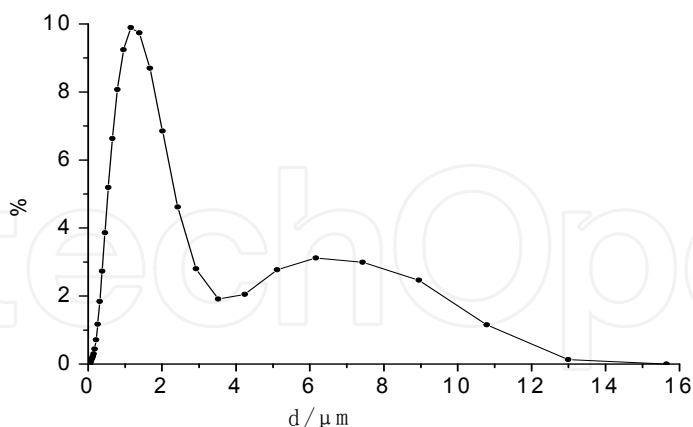

Fig. 2. EDAX of roasted Al$_2$O$_3$ powder

Fig. 3. Particle size distributions of Al$_2$O$_3$ powder

In the ZrO$_2$-TiB$_2$-Al$_2$O$_3$ nano composite ceramic tool and die material system, Al$_2$O$_3$ as the reinforcement phase in ZrO$_2$ ceramic, chemical reaction does not occur. But under the high temperature, TiO$_2$ may be formed by the direct reaction between TiB$_2$ and ZrO$_2$ or Al$_2$O$_3$ which is bad to the mechanical properties. The possible reactions are as follows:

$$TiB_2 + ZrO_2 = ZrB_2 + TiO_2 \tag{1}$$

$$2TiB_2+Al_2O_3=2AlB_2+TiO+TiO_2 \tag{2}$$
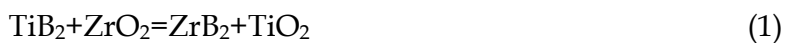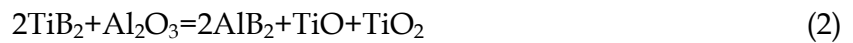
Using the data in the handbook of thermodynamic data of inorganic compounds, the standard reaction Gibbs free energy of reaction (1) and (2) at 1900K are 142.91 KJ / mol and 697.97 KJ / mol, respectively. Based on the minimum free enthalpy principle, the two reactions do not occur at 1900K. The result shows that the ZrO_2-TiB_2-Al_2O_3 nano composite ceramic tool and die material has good chemical compatibility. Fig. 4 shows the X ray diffraction before and after sintering composites.
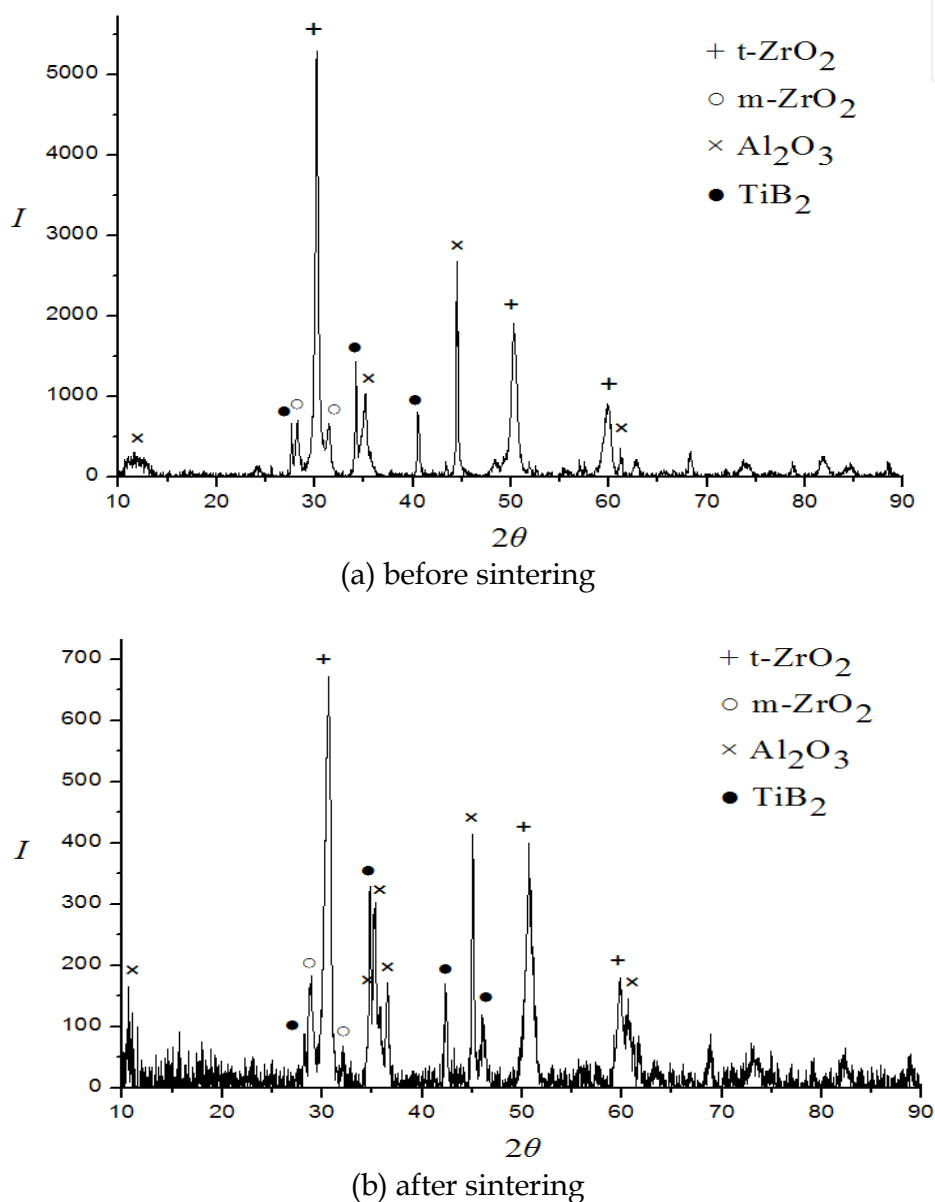

(a) before sintering

(b) after sintering

Fig. 4. XRD of the ceramic composites

As shown in Fig. 4, the phase of material had not obviously change before and after sintering. It proved that the composites have good chemical compatibility.

ZrO_2, TiB_2 and Al_2O_3 were mixed together for 48h by milling using cemented carbide balls. After milling, the slurry was dried in vacuum and screened. The mixture was hot pressed in

a graphite mold at 1430°C in vacuum with the time duration of 60min and pressure of 35MPa. Composite material was made into 4mm×3mm×36mm standard sample after cutting and polishing. The flexural strength was measured by three-point bending method with a span of 20mm and loading rate of 0.5mm/min. The hardness was measured by Hv-120 Vickers hardness tester under the load of 196N for 15s. Fracture toughness was measured by the indentation method. The microstructure and phase of the composite were analyzed with environmental scanning electron microscope (ESEM, model FEI-quanta 200) and X-ray diffraction (XRD, model BRUKER D8).

The wear test was carried on the MMW-1A configuration control multi-purpose friction abrasion tester, using pin on disc form. For the actual operating conditions, 45# chilled steel rings were selected as the friction pair material. The outer diameter and the inside diameter is Ø54mm and Ø38mm, respectively with 10mm high. The hardness of the workpiese material is 44~46HRC with the surface roughness Ra=0.4µm.

According to the request of wear tester, material was made into 10mm×10mm×15mm standard sample after cutting and polishing, and the opposite surface (10mm×10mm surface) which do the friction attrition experiment was polished to the surface roughness Ra=0.1µm. After polishing, the sample is dipped into acetone and cleaned with ultrasonic washer for 5min. Finally, it is dried in vacuum for 24h.

In the experiment, the sliding dry friction was carried out without any lubricant. The normal load was 160N and the rotational speed was 200r/min. Under this condition, dry friction wear tests of the ZrO_2 nano-composites have been carried out. The friction coefficient can be obtained by directly reading in the experiment process. The data were read at 5min after the friction starts and a measured value was taken at intervals of 10min. A total of five measurements were taken to calculate the average as the final result. The wear rate was calculated by expression. The friction and wear appearance of the briquette polishing scratches surface was carried on FEI-quanta 200 environmental scanning electron microscope (ESEM).

3. Preparation of ZrO_2-TiB_2-Al_2O_3 nano composite ceramic too and die material

3.1 Components and mechanical property of ceramic material

In order to improve the comprehensive mechanical properties of ZrO_2 ceramic material, the influence of different particle size and contents of TiB_2 and Al_2O_3 powders on the microstructure and mechanical properties of ZrO_2 nano composite ceramic tool and die material is investigated. ZrO_2 nano composite ceramic tool and die material is prepared with Vacuum hot pressing technique at 1 450 °C for 60 min at 30 MPa. The results were shown in the Table 1.

As shown in Table 1, the fracture toughness of the composite is good, but the flexural strength and hardness is low. The flexural strength, the fracture toughness and the hardness of the ceramic material reaches 619MPa, 12.2MPam$^{1/2}$ and 10.71GPa, and the composites with 10 vol. % Al_2O_3 and 10 vol. % TiB_2 has the optimum comprehensive mechanical property.

Materials	Fracture toughness /MPa·m$^{1/2}$	Hardness /GPa	Flexural strength/MPa
ZB(5)A(5)	9.76	10.03	619
ZB(5)A(10)	10.59	10.20	501
ZB(5)A(15)	9.95	10.36	509
ZB(10)A(5)	10.51	10.37	617
ZB(10)A(10)	11.37	10.71	612
ZB(10)A(15)	12.20	10.19	565
ZB(15)A(5)	7.86	9.82	513
ZB(15)A(10)	7.91	10.22	524
ZB(15)A(15)	8.11	10.14	520

Table 1. Mechanical properties of the ceramic tool and die materials

Table 2 shows the mechanical properties of ZrO_2 nano composite ceramic tool and die material with different sized Al_2O_3 powders. The flexural strength and hardness of the composites with micrometer sized Al_2O_3 powders is higher than that with nanometer sized Al_2O_3 powders, but the fracture toughness is lower than the latter. In ZrO_2 nano composite ceramic tool and die material, ZrO_2 transformation toughening effect is the main toughening mechanism, the effect of Al_2O_3 on mechanical property is due to the particle reinforcement [Elshazly et al, 2008]. Nanometer sized Al_2O_3 has pinning effect on the grain boundary, restrictions the grain boundary sliding, this is propitious to make the matrix grain finer and is good for the fracture toughness. The grain size of the composite with micrometer sized Al_2O_3 is bigger than that with nanometer sized Al_2O_3, but the effect of particle reinforcement is higher than the latter, this is the main reason of the higher flexural strength.

Material	Flexural strength /MPa	Fracture toughness /MPa·m$^{1/2}$	Hardness /GPa
With micro- Al_2O_3	743	7.75	11.6
With nano- Al_2O_3	612	11.37	10.71

Table 2. Mechanical properties of the ceramic with different sized Al_2O_3 powders

Fig.5 shows the SEM morphology of ZrO_2 nano composite ceramic tool and die material with different sized Al_2O_3 powders. The microstructure of the composite with nanometer sized Al_2O_3 powders is finer than that with micrometer sized Al_2O_3 powders.

The results showed that the highest flexural strength of ZrO_2-TiB_2-Al_2O_3 nano-composite ceramic tool and die material reaches 743 MPa with 10 vol. % Al_2O_3 micrometer sized powders. The fracture toughness increased obviously along with the increase of Al_2O_3 nanometer sized powders, and reaches 11.37 MPa·m$^{1/2}$. Vickers hardness did not change obviously with different Al_2O_3 powders, while it greatly increased with the increases of Al_2O_3 content.
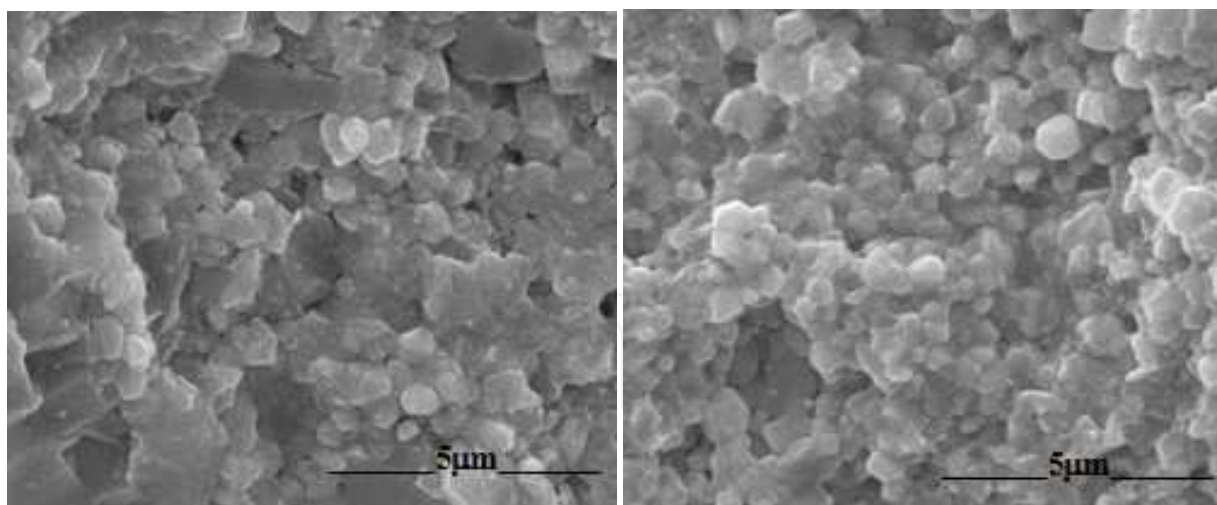
(a) with micrometer sized Al_2O_3 powder   (b) with nanometer sized Al_2O_3 powders

Fig. 5. SEM of the composites with different sized Al_2O_3 powders

3.2 Hot pressing technology of ceramic material

3.2.1 Effects of holding time

Fig. 6 shows the effect of holding time on the flexural strength of ZrO_2 nano-composite ceramic tool and die material when sintered at 1 450 °C. It can be seen from Fig. 6 that the flexural increases first and then decreases with the increase of holding time, reaching the maximum of 878 MPa when the holding time is 60 min. Fig. 7 shows th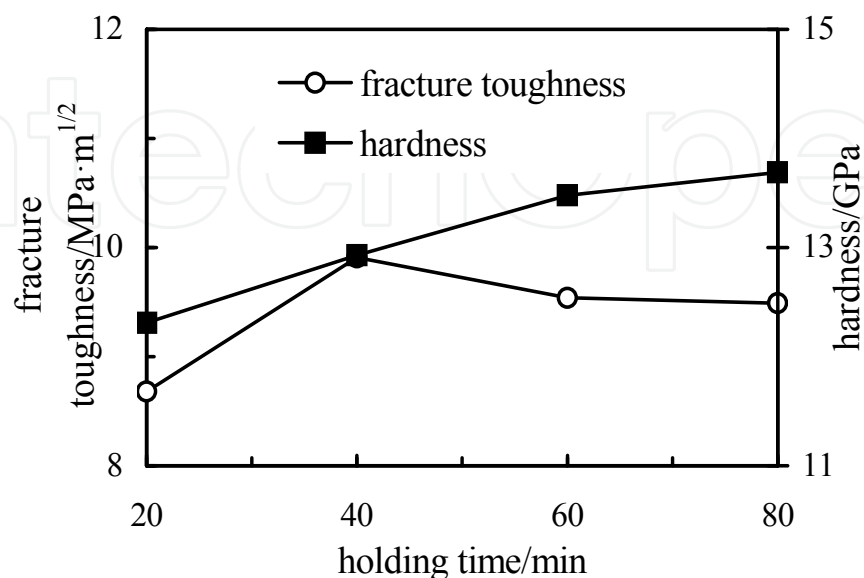e effect of holding time on the fracture toughness and hardness of the composite material. The hardness increases with the increase of the holding time, reaching the maximum of 13.48 GPa when the holding time is 80min. Fracture toughness increases and then decreases with holding time increases, reaching the maximum of 9.91 $MPa \cdot m^{1/2}$ when the holding time is 40min.

Fig. 8 shows the SEM morphologies of ZrO_2 nano-composite ceramic tool and die material with the holding time of 20min, 60min and 80min. It can be seen from Fig. 8, the microstructure of the composite material has changed greatly with the holding time increases, and to be the best when the holding time is 60 min. The reason is that proper holding time can improve the microstructure, ceramic material becomes further densification when the holding time is 60 min, and many nano-meter sized grains has found in the grain boundary which contribute to the trans/inter-granular mixed fracture mode occurs.

As a result, the flexural strength and fracture toughness of the composite material when the holding time is 60min are better than the other holding time.

Fig. 9 shows the effects of hot pressing temperature on the flexural strength of ZrO_2 nano-composite ceramic tool and die material with the holding time of 60min. The flexural strength first increases and then decreases with the increase of hot pressing temperature from 1420 °C to 1470 °C, and reaching the maximum of 1055 MPa at 1430 °C. Fig.10 shows the effects of hot pressing temperature on the fracture toughness and hardness. As shown in Fig. 10, the change of the hardness and the fracture toughness are nearly the same in trend

as that of the flexural strength, the hardness reaching the maximum of 13.78 GPa when the hot pressing temperature of 1460 °C and the fracture toughness reaching the maximum of 10.57 MPa m$^{1/2}$ when the hot pressing temperature is 1430 °C. It can be seen that the effect of sintering temperature on the mechanical properties of the composite material is obvious, proper hot pressing temperature can improve the mechanical properties, the flexural strength and the fracture toughness respectively reaching the maximum of 1055 MPa and 10.57 MPa m$^{1/2}$ at 1430 °C and the hardness of this sintering temperature is lower than the maximum.
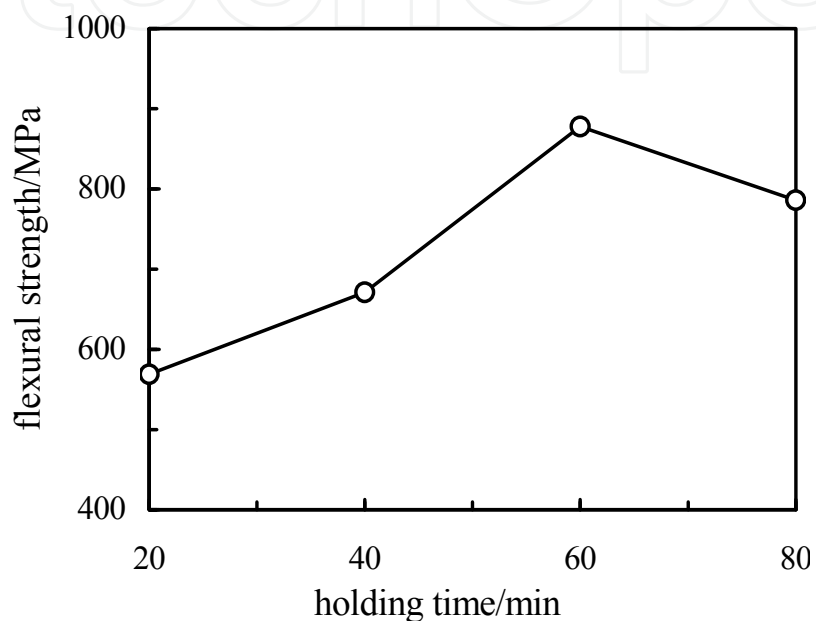
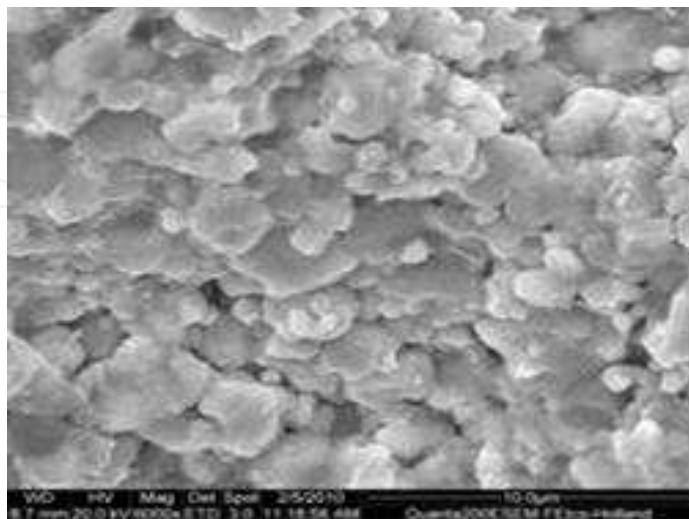Fig. 6. Effects of holding time on the flexural strength

Fig. 7. Effects of holding time on the fracture toughness and hardness
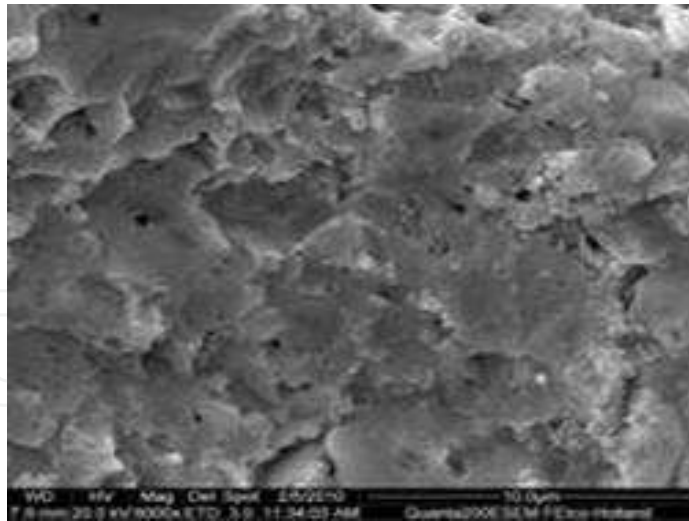
(a) remain 20min at 1450 °C
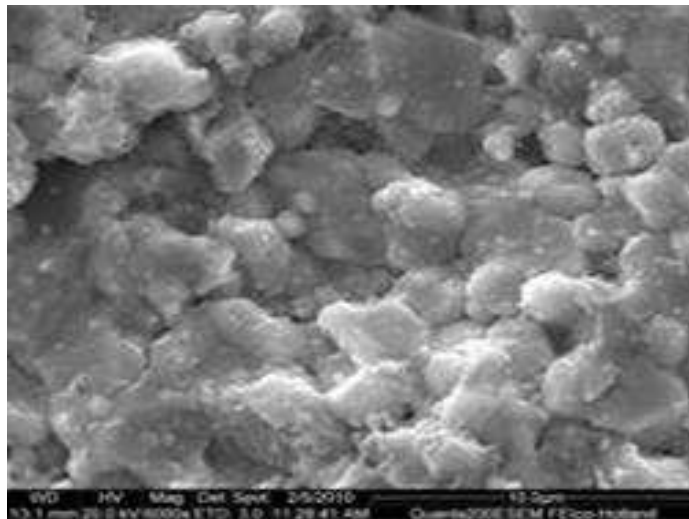
(b) remain 60min at 1450 °C

(c) remain 80min at 1450 °C

Fig. 8. SEM morphologies of the ceramic tool and die material under different holding times
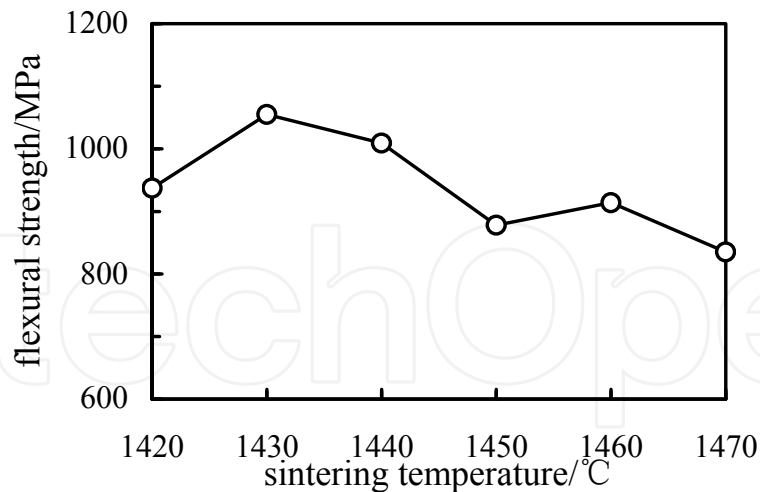
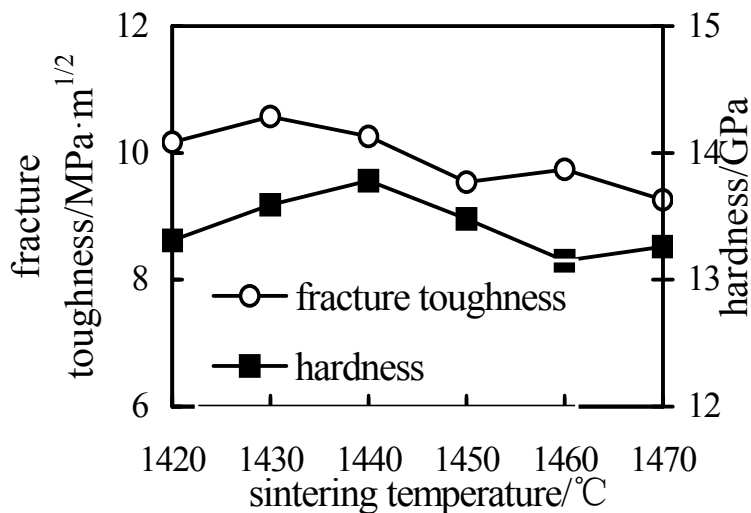Fig. 9. Effects of hot pressing temperature on the flexural strength

Fig. 10. Effects of hot pressing temperature on the fracture toughness and hardness

Fig. 11 shows the SEM morphologies of the ZrO_2 nano-composite ceramic tool and die material sintered at the temperature of 1420 °C, 1430 °C and 1450 °C, with the holding time of 60 min. It can be seen from Fig. 11 that the microstructure of the tested ZrO_2 nano-composite ceramic tool and die material is a typical kind of the intragranular/intergranular microstructure and the fracture mode is the mixture of both transgranular/intergranular fracture, and the mixture of both transgranular/ intergranular fracture occurred at 1430 °C is better than that which was sintered at 1420 °C, this is the main reason for the high mechanical properties. Compared to the Fig.11(c), the microstructure of the composite materials at 1420 °C and 1430 °C are obviously finer than that which was sintered at 1450 °C. The abnormal grains which can be found in Fig.11 (c) could affect the mechanical properties of the composite material.
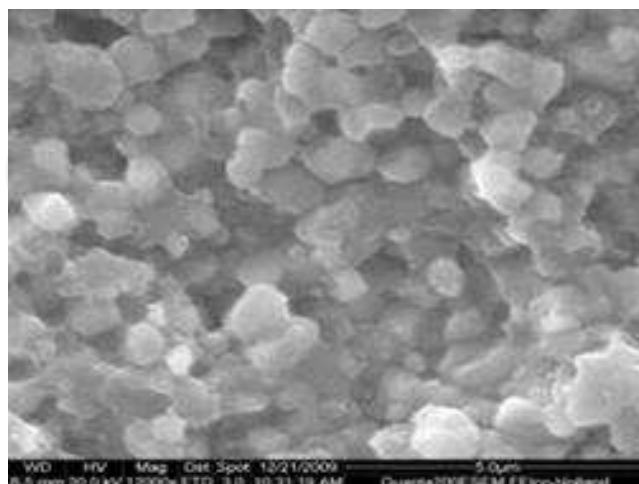
Therefore the appropriate sintering temperature of ZrO_2 nanocomposite ceramic tool and die material is 1430 °C.
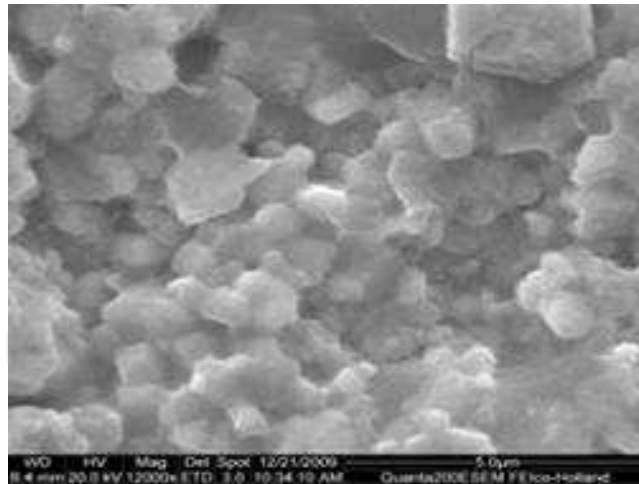
(a) 1420 °C
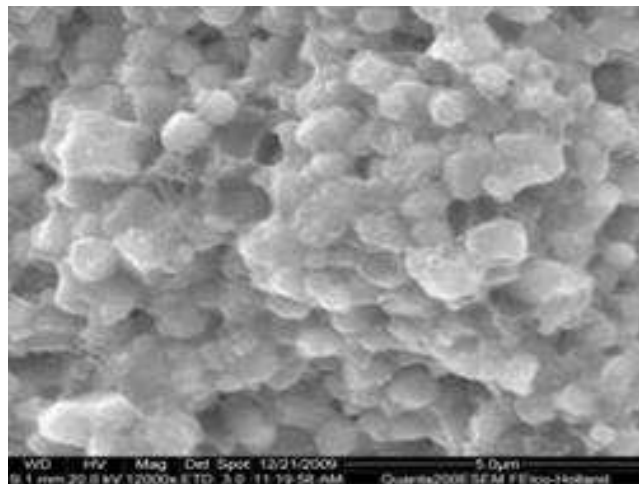
(b) 1430 °C

(c) 1450 °C

Fig. 11. SEM morphologies of the ceramic tool and die material under different hot pressing temperatures

3.3 Sintering process of ceramic material

Two kinds of ceramic materials were prepared by hot press technology at 1430 °C in vacuum with the time duration of 60 min and hot pressing pressure of 35 MPa. Besides, a time duration of 120 min at 1100 °C was added in composite 2. The mechanical properties of the composites are shown in Table 3.

Material	Flexural strength /MPa	Fracture toughness /MPa·m$^{1/2}$	Hardness /GPa
Composite 1	765	8.18	11.6
Composite 2	878	9.54	13.48

Table 3. Compositions and mechanical properties of the ceramic tool and die materials

It indicates that 1100 °C is approach the transformation temperature when the crystal structure of zirconium dioxide is transformed from monoclinic to tetragonal. This process also follows about 7% volume contraction. The nano-meter sized grains grow up generally after 1200 °C. Keeping on hot pressing a period of time at this temperature firstly can make the crystal structure of zirconium dioxide be transformed from monoclinic to tetragonal; The second, it also can accelerate the sintering densification when the grain growth is not obvious which is benefit to obtain a more ideal microstructure and mechanical property of the nano-composite ceramic material.

As shown in Table 3, composite 2 has the same components and sintering process with composite 1 except this 120 min is sintering at 1100 °C, but all the mechanical properties are noticeably higher than that of composite 1.

Investigation on the Vickers indentation is one of the effective methods to characterize the change of hardness and toughness. Fig. 12 shows the morphologies of Vickers indentation of both composite 1 and 2. As shown in Fig. 12 (a) and (b), the Vickers indentation of composite 2 is smaller than that of the composite 1 and the cracks of composite1 are obviously. It indicates that this sinter process can enhance the hardness of ZrO_2 ceramic materials. As shown in Fig. 12 (c) and (d), the crack of composite 2 is shorter and thinner than that of composite 1, which suggests that the fracture toughness of composite 2 is higher than that of composite 1 obviously.

As shown in Fig. 12 (c) and (d), although the mechanical property of two materials has changed, the grain size and the distribution of Al_2O_3 and TiB_2 are similar. It indicates that the enhancement of mechanical properties is mainly because the addition of ZrO_2 and its phase transformation. These results suggest that keeping sintering of 120 min at 1100 °C can make all of the ZrO_2 phase be transformed from monoclinic to tetragonal. It is a volume expansion process when the ZrO_2 grains transforms from tetragonal symmetry to monoclinic symmetry. It is very difficult to make the tetragonal be transformed to monoclinic resulted from the high hot pressing pressure. Thus, most of the tetragonal ZrO_2 grains can be kept after finish sintering until the room temperature.

When a crack appears and extends through the ZrO_2 grains, the tetragonal grains will be transformed to monoclinic under the stress of crack tip. On the one hand, this process can absorb the fracture energy and reduce crack tip stress; on the other hand, phase

transformation often follows by the volume expansion which can press the crack tip and cause the crack thinning or even stop extending. This process is the typical stress-induced transformation toughening.
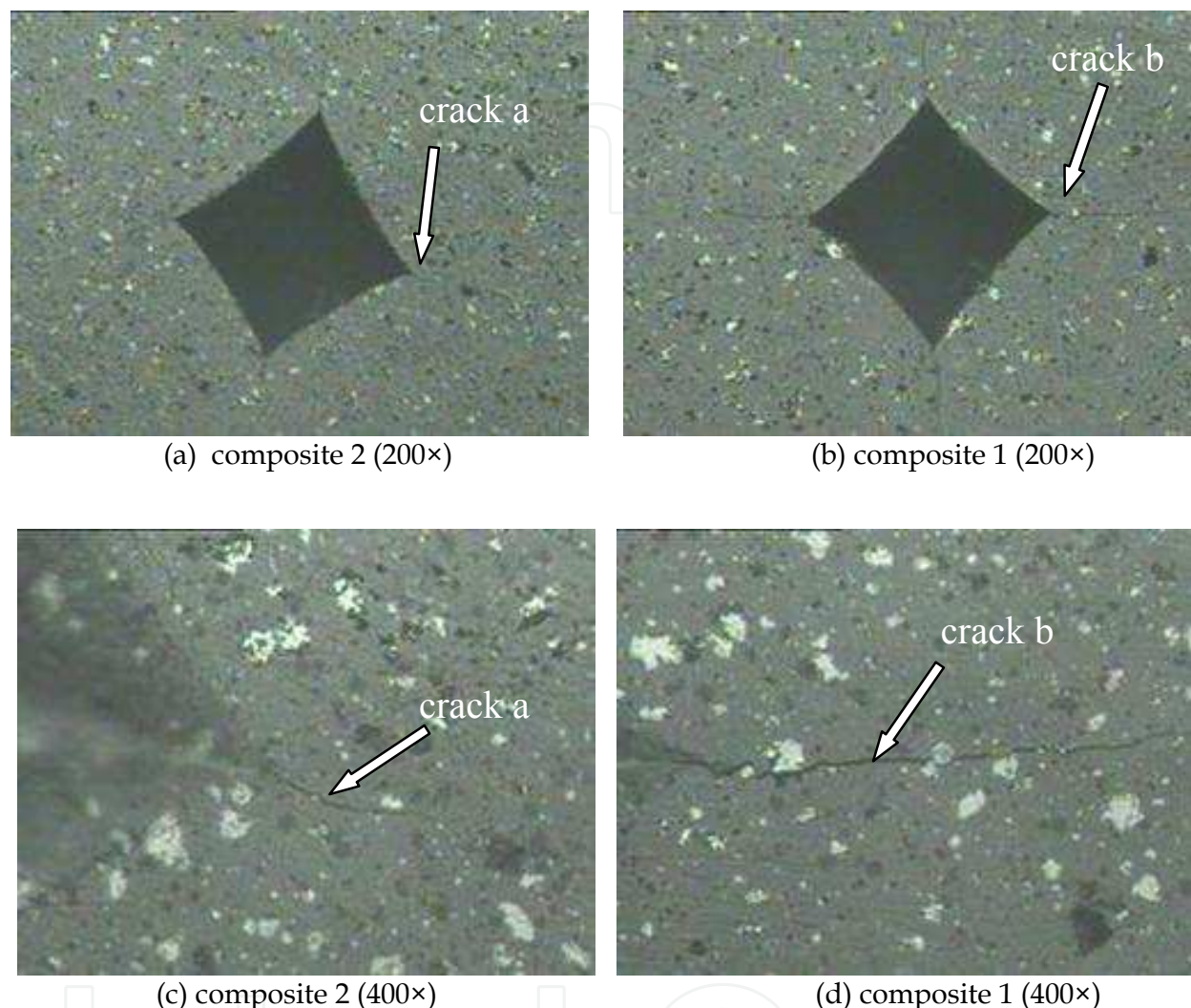

(a) composite 2 (200×)   (b) composite 1 (200×)

(c) composite 2 (400×)   (d) composite 1 (400×)

Fig. 12. Morphologies of Vickers indentation

In order to study the change of phase transformation, the material surface is analyzed by XRD. As shown in Fig. 13(a) and (b), two diffraction peaks appears in nearby 30° after the common sintering process, which is the monoclinic ZrO_2. After the optimal sintering process, the monoclinic ZrO_2 disappeared, and all of the ZrO_2 grains are tetragonal symmetry.

Microstructure of both composite 1 and 2 materials under SEM are shown in Fig. 14. It can be seen that grains in composite 2 are finer than that in composite 1. Most of the composite 1 material grains are about 200 nm while the composite 1 material only has few of fine grains distributed in the grain boundary. The finer the grain is, the higher the mechanical property of nano-meter composite ceramic material is. After 120 min sintering at 1100 °C, materials have reached nearly the fall densification which can limit the grain growth space.
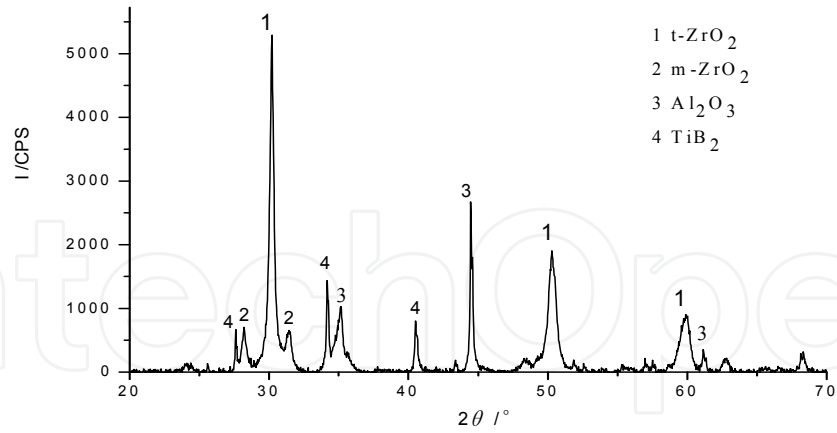
(a) mixed powder
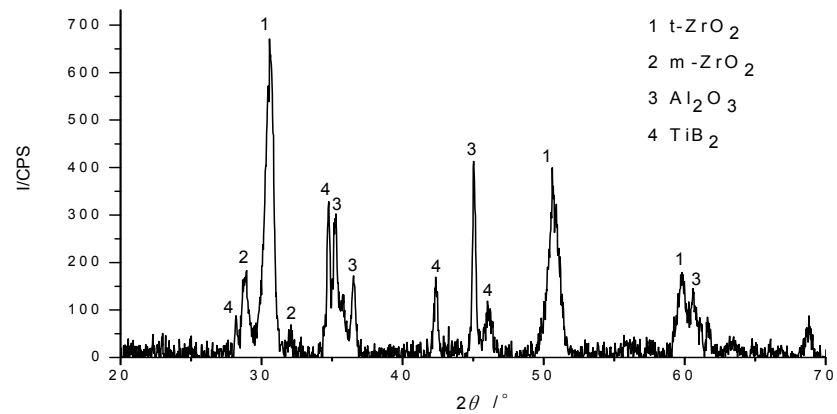
(b) common sintering process
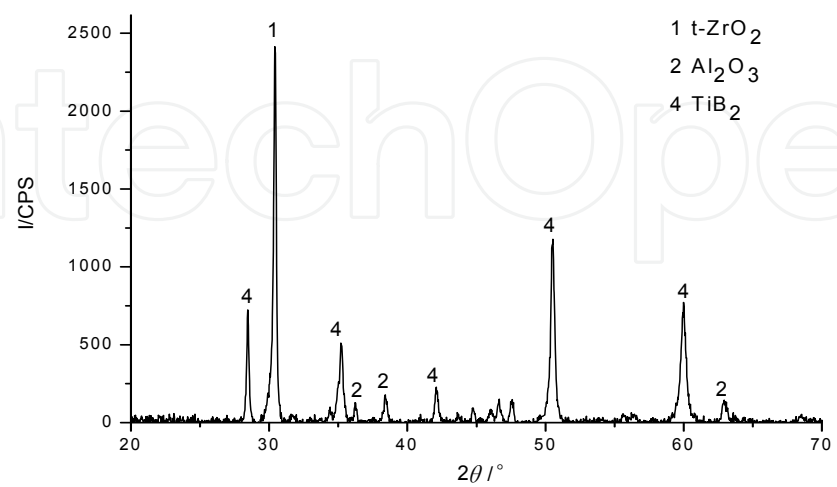
(c) optimal sintering process

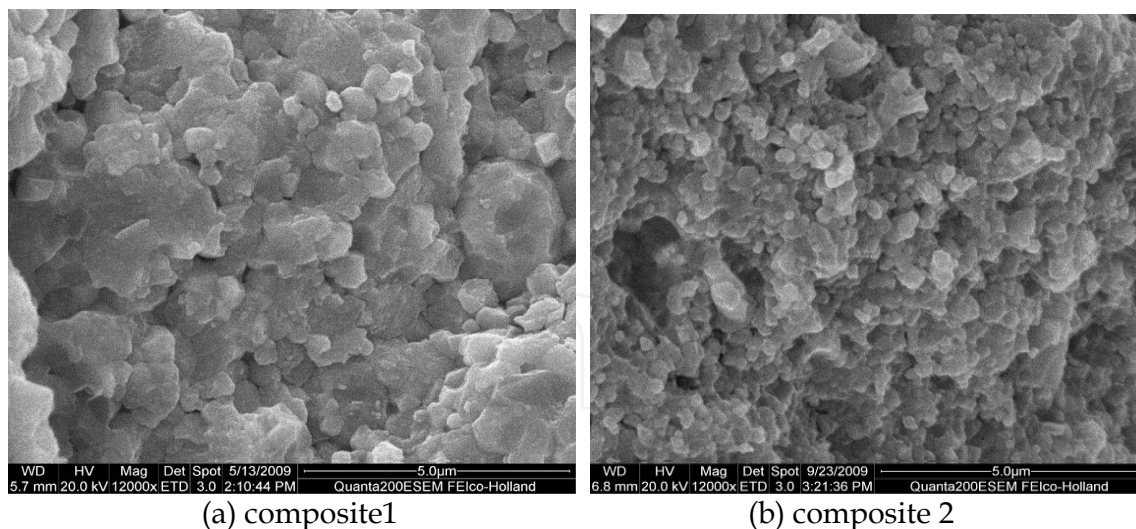Fig. 13. XRD analysis of nano-composite ceramic tool and die material

(a) composite1   (b) composite 2

Fig. 14. SEM morphology of the composites with different sinter process

4. Tribological design of ZrO$_2$ nano-composite ceramic tool and die material

In this experiment, the mechanical properties of ZrO$_2$ nano-composites can be seen from Table 4.

Material	TiB$_2$ /Vol. %	Al$_2$O$_3$ /Vol. %	Fracture toughness /MPa·m$^{1/2}$	Hardness /GPa	Flexural strength /MPa
a	5	10	10.59	10.20	501
b	10	5	10.51	10.37	617
c	10	10	11.37	10.71	612
d	10	15	12.20	10.19	565
e	15	10	7.91	10.22	524

Table 4. Compositions and Mechanical properties of ZrO$_2$ nano-composites

Fig.15 shows the friction coefficient and the wear rate of different TiB$_2$ contents under the 200r/min rotational speed and the load of 160N. The result shows that the friction coefficient of the composites decreases with the increase of TiB$_2$ content, reaches the minimum when TiB$_2$ content amounts to be 15 vol. %. The wear rate of the composites decreases first and then increases with the increase of TiB$_2$ content, reaches the minimum of 1.29×10^{-6} mm^3/N·m when TiB$_2$ content amounts to be 10 vol. %.

Contrast Fig.15 with Table 4, the changing trends of the friction and wear properties and the mechanical properties of the composites are roughly the same. The results indicated that the proper additive of TiB$_2$ could improve both the friction and wear properties and the mechanical properties. Different TiB$_2$ contents will significantly affect density of the material, and then the density directly affects the mechanical properties of materials. Although the additive of TiB$_2$ could improve the friction and wear properties, the high TiB$_2$ content also affect the microstructure of materials and the surface of materials was easy to be broken, and is bad for the friction and wear properties.
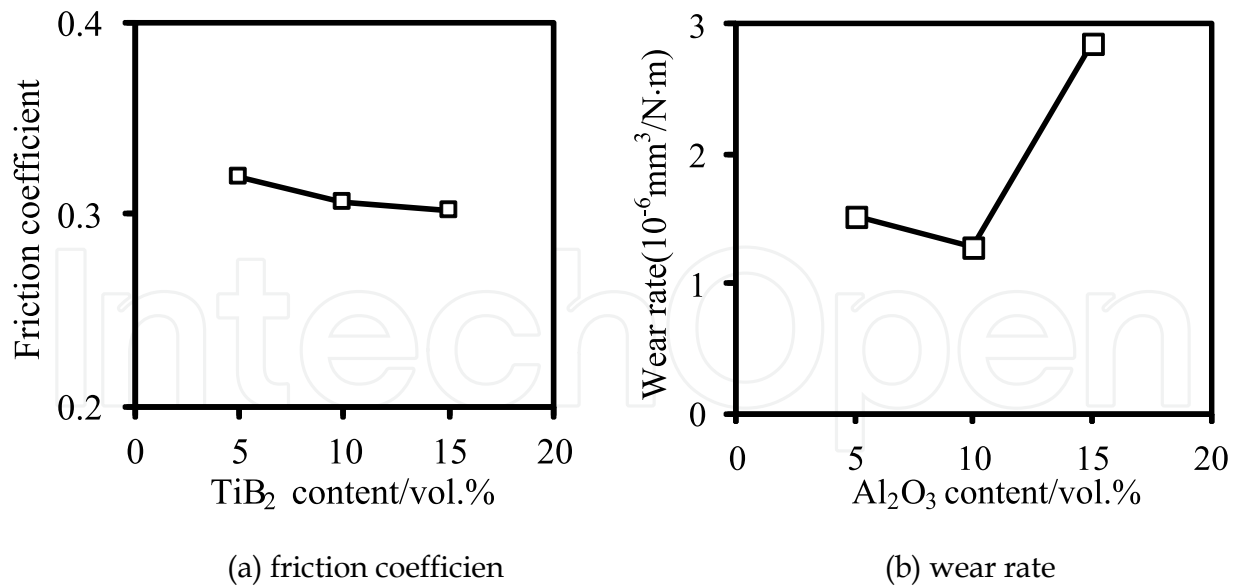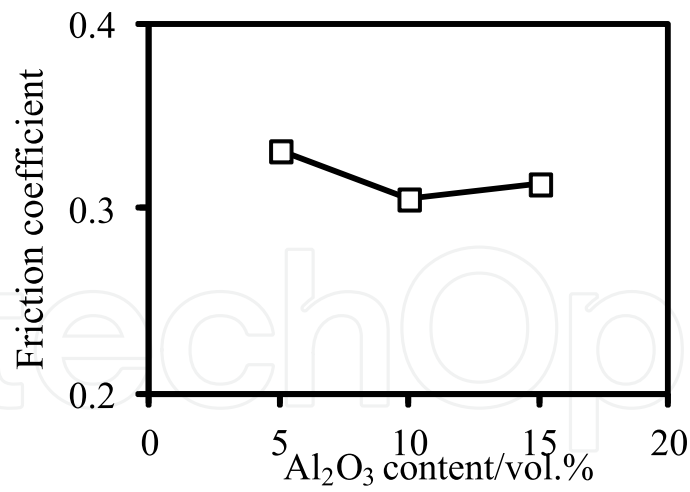
(a) friction coefficien   (b) wear rate

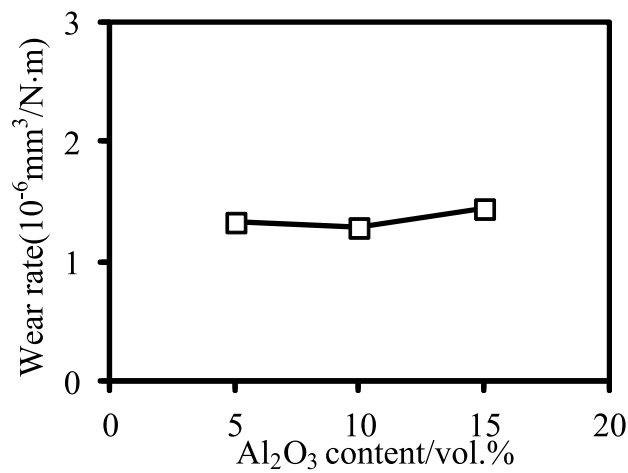Fig. 15. Effect of different TiB$_2$ contents on friction coefficient and wear rate

Fig.16 shows the friction coefficient and the wear rate of different Al$_2$O$_3$ contents under the 200r/min rotational speed and the load of 160N. The result shows that the friction coefficient of the composites decreases first and then increases with the increase of Al$_2$O$_3$ content, reaches the minimum when Al$_2$O$_3$ content amounts to be 10 vol. %. As the content of Al$_2$O$_3$ increases, the change of the wear rate is nearly the same in trend as that of the friction coefficient but not obvious, reaching the minimum of 1.286×10^{-6} mm^3/N·m when Al$_2$O$_3$ content amounts to be 10 vol. %. Al$_2$O$_3$ is proved a strengthening material of ZrO$_2$, the microstructure and the density of materials were obtained by the addition of Al$_2$O$_3$ particles, thus the mechanical properties of materials are increased, and reaches the maximum when Al$_2$O$_3$ content amounts to be 10 vol. % (Table 4),and with increasing Al$_2$O$_3$ content (from 5 vol. % to 10 vol. % in composites), the friction and wear properties of ZrO$_2$ composites are continuely increased, but increasing Al$_2$O$_3$ content further (up to 10 vol. %), it is decreased.

The effect of material content on the friction and wear properties of the composites is obviously, proper material content not only increase the mechanical properties, but also improve the friction and wear behaviors. Compared with friction coefficient, the changing trends of wear rate with mechanical properties is obviously, the reason is that both of the good wear rate and well mechanical properties needed the finer microstructure, and the friction coefficient are mainly dependent on the TiB$_2$ content [Mazaheri et al, 2008].

Fig.17 shows that the surface of the composite is smooth and a small amount of defect area can also be observed. The smooth surface is mainly because of the friction between the ceramic material and the steel ring. The friction chip has high surface activity and easy adheres to the material surface, forming the continual surface layer on the surface with the increase of wear time. The smooth and continue surface layer can effectively reduce the coefficient and slow the wear. With the temperature of friction area increase, wear increase because of the plastic deformation and material transfer take place, form the adhesive wear.
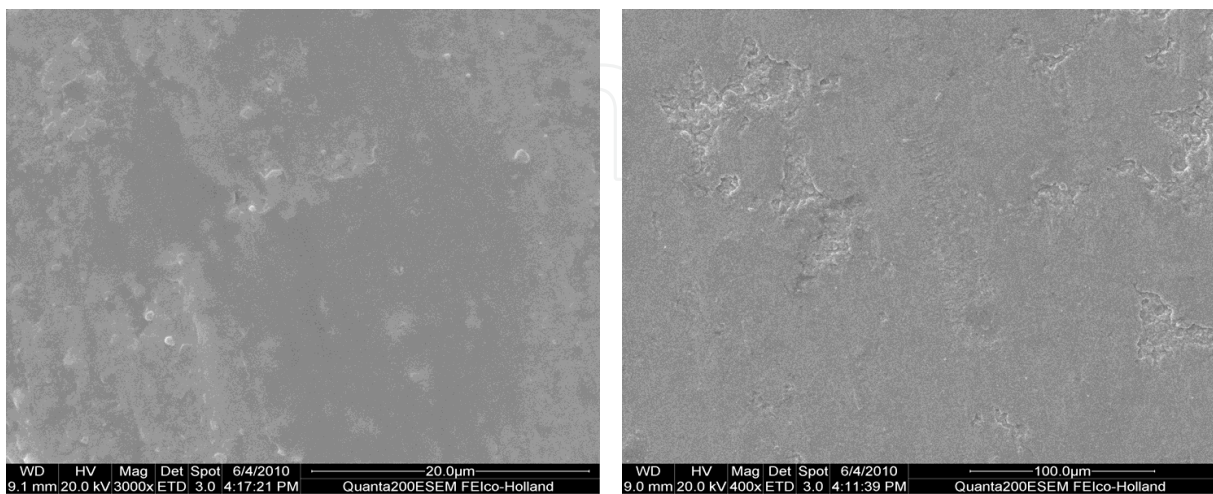
(a) Friction coefficient

(b) Wear rate

Fig. 16. Effects of different TiB$_2$ content on friction coefficient and wear rate


(a) 3000×   (b) 400×

Fig. 17. SEM morphologies of ZrO$_2$ nano-composite ceramic tool and die material

XRD was used to analyze the physics of surface film(Fig.18). More TiB_2 and Al_2O_3 can be seen from Fig.18(b), the main reason is that the hardness of TiB_2 and Al_2O_3 is higher than ZrO_2 and this can reduce the wear in friction. Secondly, TiB_2 is proved a self-lubricating material which can low friction coefficient. Besides, FeO was found on the material surface after the test (Fig.18(b)), this was come from the reaction between the steel chip and the atmosphere under the friction heat and moved by friction. The softer FeO chips and the ceramic chips were mixed by the mechanical pressure, formed the surface layer which can protect the ceramic material and reduced the wear.
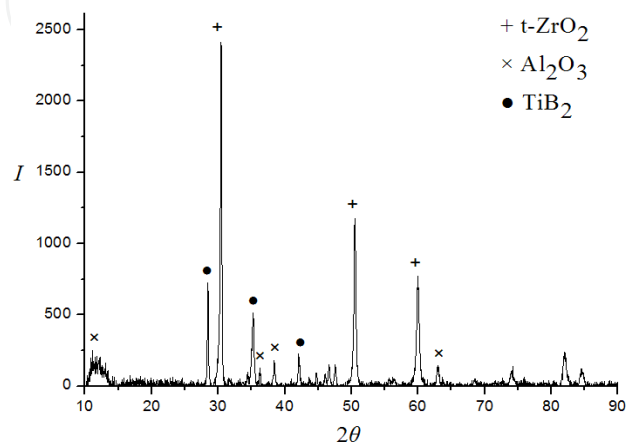
(a)before the test
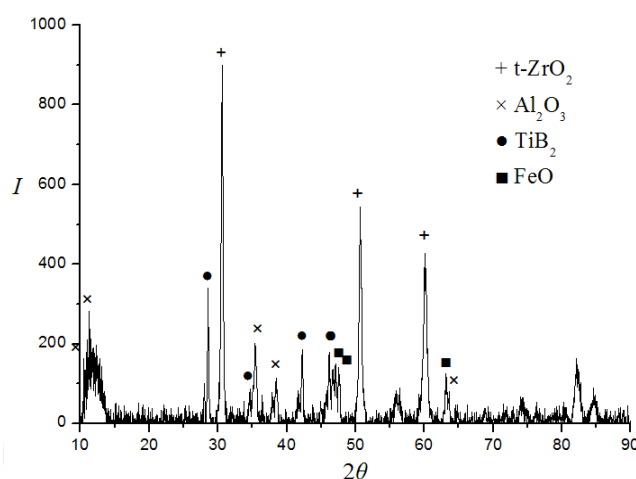
(b) after the test

Fig. 18. XRD analysis of ZrO_2 nano-composite ceramic tool and die material

5. Friction and wear behaviour

Fig.19 shows the effects of load and rotational speed on the friction coefficient of composites. The friction coefficient of the composites first and then decreases with the increases of load under the 200r/min rotational speed, and the friction coefficient of the composites decreases with the increases of rotational speed under the 160N load. The friction coefficient reaches the minimum of 0.3 and 0.29 when the load is 240N and the rotational speed is 200r/min, respectively.
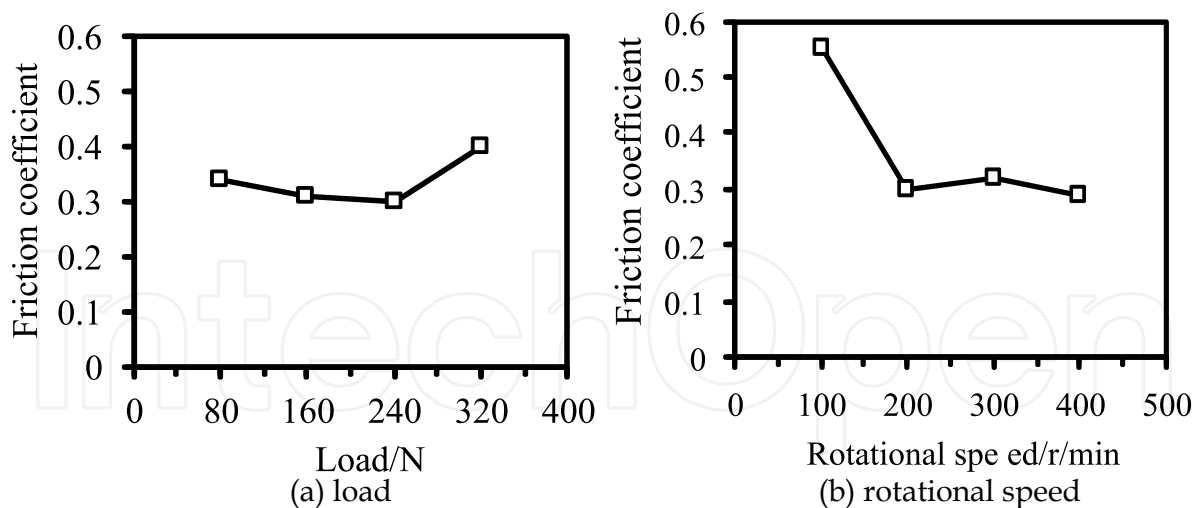
Fig. 19. Effects of load and rotational speed on the friction coefficient

Fig.20 shows the effects of load and rotational speed on the wear rate of composites. The change of wear rate is near the same with the friction coefficient. The wear rate decreases with the load from 80N to 240N under the 200r/min rotational speed, but when the load increases to 320N, the wear rate reach the maximum, 5.44×10^{-6}mm^3/N·m. The wear rate decreases with the speed increase as can be seen in Fig.20(b).

Fig.21 shows the SEM of the wear surface with 160N and 200r/min. The surface is smooth and most of the surface is covered by a nearly continuous layer in Fig. 21(a). The wear appearance of ceramic surface mainly includes two parts, part 1 is a smooth and grey area (point 1 in Fig.21), part 2 is the saddle(point 2 in Fig.21). In order to attribute the phase differences of the two parts, the EDAX electron spectrum analysis was carried out. Fig.21 (a) and (b) shows the electron spectrum analytic curve of point 1 and point 2.

As can be seen from Fig. 22, main elements come from the composite ceramic material. A few Fe exist obviously in point 1, but no Fe element can be found in point 2. Fe comes from the 45# steel work-piece. The chips which produced in the friction process has the high activeness, easily adheres in the friction surface and some shifted to the ceramic surface along with the friction process. After the progression rolling, the mix chips forms a soft and continuous film on the ceramic surface.

XRD was used to analyze the phase change in the friction. Fig.23 shows the XRD of the material surface before and after the wear test. FeO can be found on the ceramic surface after the friction(in Fig. 23(b)), and it came from the reaction between Fe and oxygen of air. The results indicated that the layer united by the work piece materials and ceramic materials. In addition, more TiB$_2$ were found on the ceramic surface. TiB$_2$ is a self-lubricating material and harder than the matrix material. Along with the friction, the TiB$_2$ content was become more and slow down the wear aggravation.

Defects also can be found from the film (point 3 in Fig. 21(b)). The colour of defects is similar to the film but obviously different from the original material. Moreover, defect is smaller and shallower than the original material. The results indicated that the material composition of the defect and film is roughly the same. Zirconium dioxide is ionic crystal, the adsorption affinity to the chip is higher. The ceramic chips mixed with workpiece chips and form the continuous film, the defect is the damage of the mixed film.
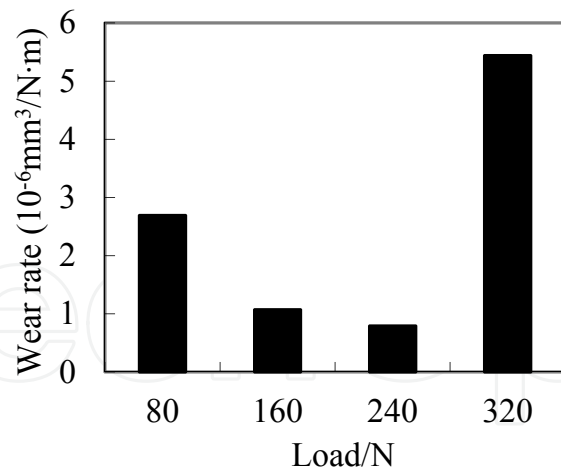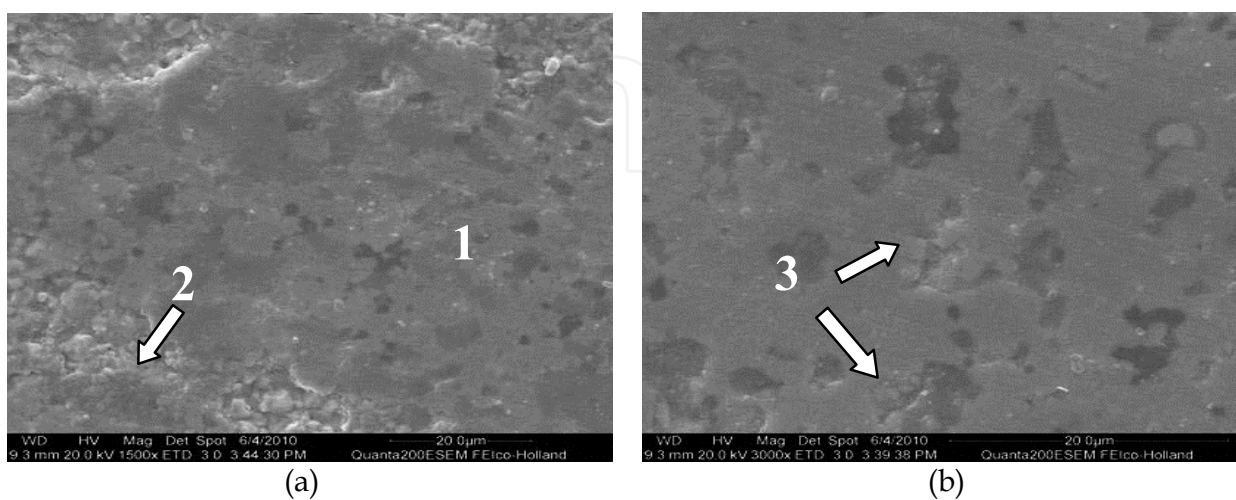
(a) load
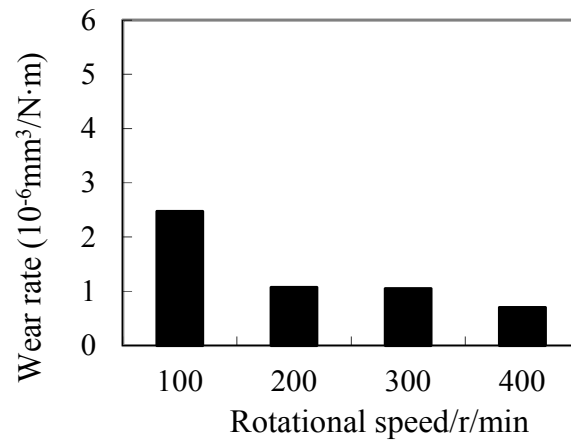
(b) rotational speed

Fig. 20. Effects of load and rotational speed on the wear rate

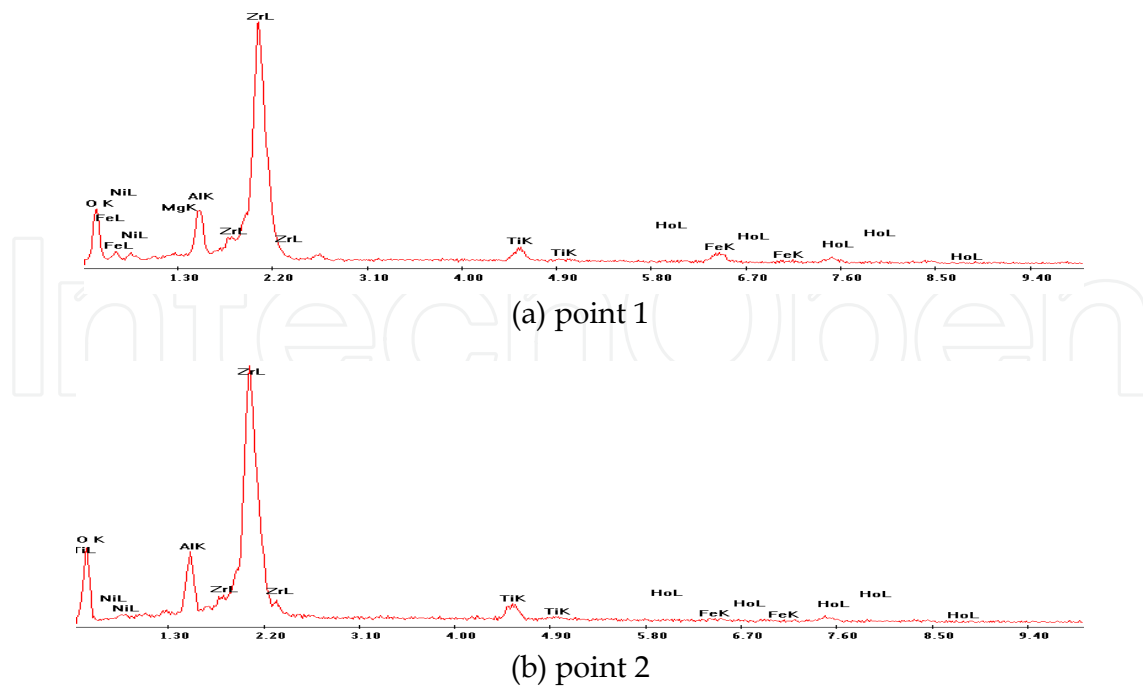Fig. 21. SEM morphologies of the wear surface with the load of 160N and speed of 200r/min

(a) point 1

(b) point 2

Fig. 22. EDAX electron spectrum of the wear surface
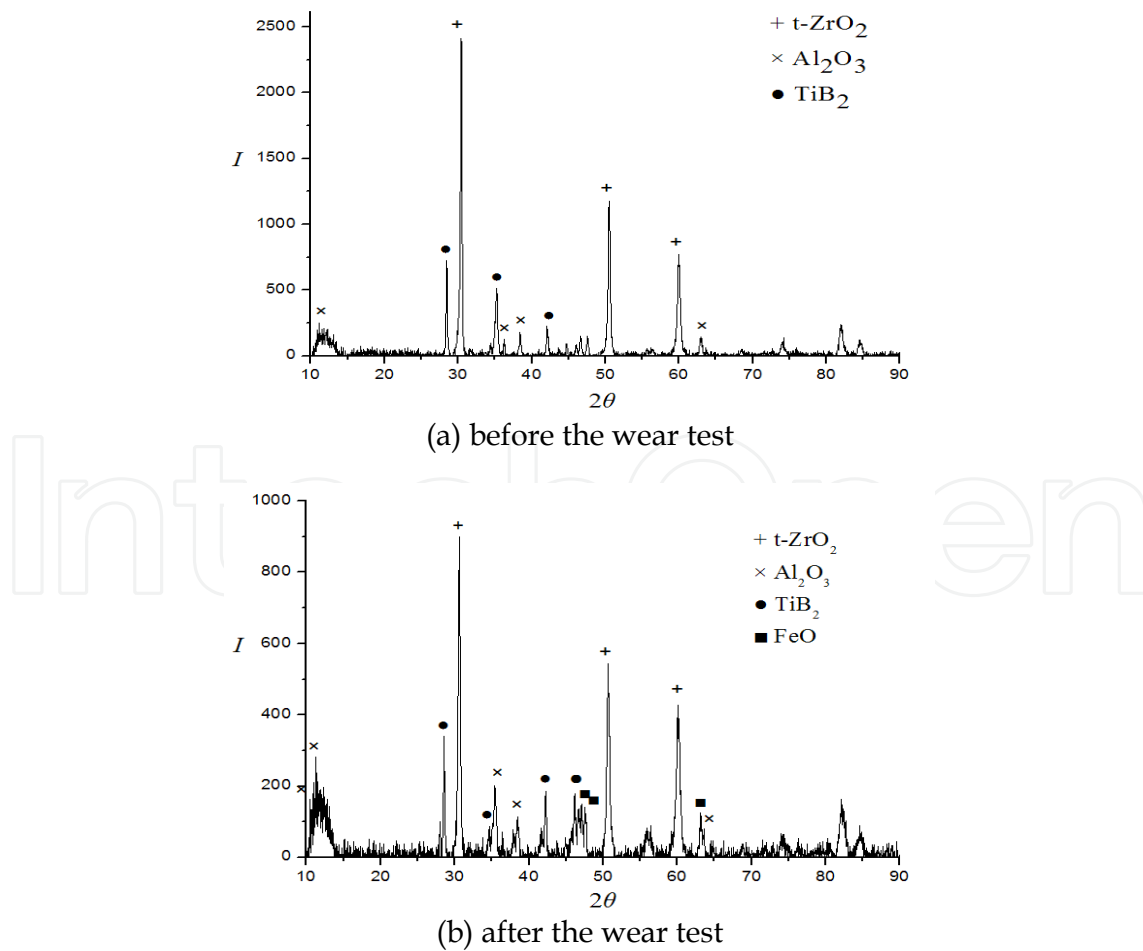

(a) before the wear test

(b) after the wear test

Fig. 23. XRD analysis of nano-composite ceramic tool and die material surface

The result shows that the soft layer was produced in the stage of adhesive wear process, the soft work-piece material chips were mixed the ceramic chips and coated on the hard composite ceramic surface under the friction. Next, the friction mainly between the soft layer and work-piece, this is the main reason of the low friction coefficient and wear rate. First, the soft layer form a continual smooth rubbing surface on the composite materials surface, and increases the actual friction contacted area, reduces the friction moment; Second, the soft layer reduce the direct contact between the work-piece and ceramic, thus slowed down the wear of composite ceramic.

Fig.24 shows the SEM morphology of the wear section of the composite when the rotational speed is 200r/min and the normal load is 160N and 320N, respectively.

(a) 160N   (b) 320N
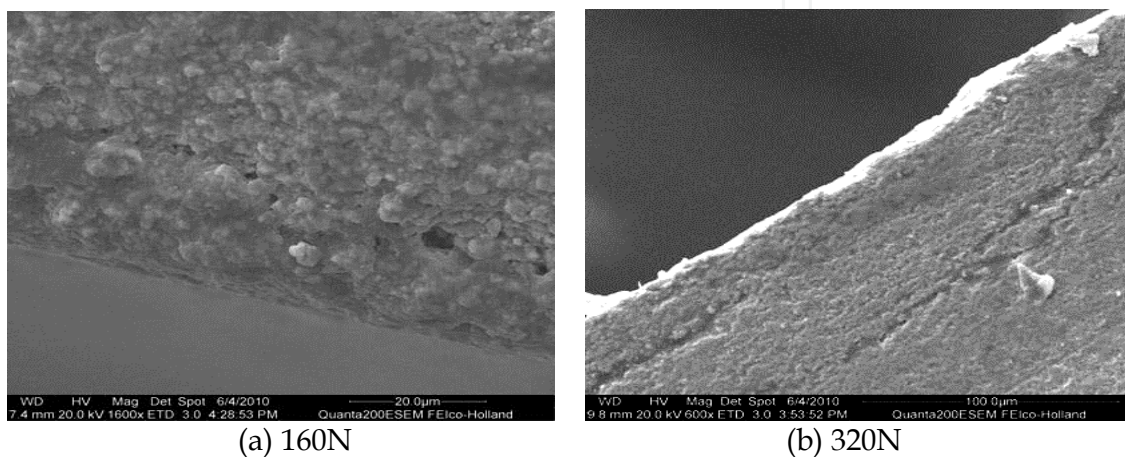
Fig. 24. SEM of the wear section with 200r/min and different load

As shown in Fig. 24(a) and (b), when the rotational speed is 200r/min and the normal load is 160N, the wear of composite ceramic is light, there is only a few flaw in the wearing course and mainly distributes in about 10 microns wear courses. The flaw is exist independently and without jointed, so it is not easy to form the serious wear as seen in Fig. 24(b).

As shown in Fig. 24(b), some transverse cracks were found in the wear layer when the load increases to 320N. The cracks could cause the wear layer broken and finally form the spalling wear. When the load is low, the wear layer does not have the obvious change, wear is mainly by the slight scuffing of ceramic, and because of the hardness of ceramic is far high than the work-piece, the wear rate is low. When the load is 320N, the wear layer is easy broken and can't effectively protect the matrix material, wear rate is higher than that in low load. The test result of wear rate can be seen from Fig.20. When the load is 160N the wear rate is $1.06×10^{-6}mm^3/Nm$. While when the load is 320N the rate of wear increases rapidly to be $5.44×10^{-6}mm^3/Nm$.

6. Conclusion

A new ZrO_2 nano-composite ceramic tool and die material was prepared by vacuum hot pressing technique. ZrO_2-TiB_2-Al_2O_3 nano-composite ceramic tool and die material with 10 vol. % TiB_2 and 10 vol. % Al_2O_3 micrometer sized powders reaches the maximum mechanical property. ZrO_2-TiB_2-Al_2O_3 nano-composite ceramic tool and die material with optimum mechanical properties can be achieved when the hot pressing temperature is

1430℃, and the holding time is 60min. The flexural strength, hardness and fracture toughness reaches 1055 MPa, 13.59GPa and 10.57MPa $\cdot$m$^{1/2}$, respectively. In the ZrO_2 nano-composite ceramic tool and die materials, the optimum sinter parameters could improve the microstructure, and the optimum sinter process could nearly completely stabilize the t-ZrO_2 to the room temperature condition that can enhance the toughening effect of ZrO_2. The additive of self-lubricating material TiB_2 could reduce the friction coefficient and improve the abrasion resistance. Moreover, the TiB_2 content was become more under the continuous friction condition which is able to slow down the wear aggravation. The continuous friction film was formed by the ceramic and work-piece chips under the friction. The film could reduce the friction and protect the matrix material. The wear rate of ZrO_2 nano-composite ceramic tool and die material is 1.06×10^{-6}mm^3/Nm when the rotational speed is 200r/min and the normal load is 160N. It indicated that this new ceramic composite have good friction and wear properties. Therefore, it can be expected that the developed ZrO_2 nano-composite ceramic material will get further application in the field of cutting tools, dies and other wear resistant parts, etc. with high wear resistance and performance.

7. Acknowledgement

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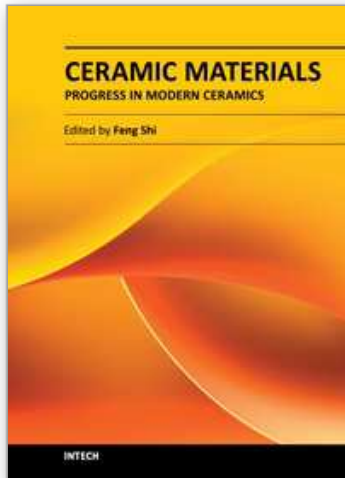
This text covers ceramic materials from the fundamentals to industrial applications. This includes their impact on the modern technologies, including nano-ceramic, ceramic matrix composites, nanostructured ceramic membranes, porous ceramics, and the sintering theory model of modern ceramics.

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