CHINESE JOURNAL OF MECHANICAL ENGINEERING
Vol. 28, No. 2, 2015

DOI: 10.3901/CJME.2015.0107.008, available online at www.springerlink.com; www.cjmenet.com; www.cjme.com.cn

# In-situ Fabricated $TiB_2$ Particle-whisker Synergistically Toughened Ti(C, N)-based Ceramic Cutting Tool Material

LIU Hanlian[1, 2, *], SHI Qiang[1, 2], HUANG Chuanzhen[1, 2], ZOU Bin[1, 2], XU Liang[1, 2], and WANG Jun[1, 2]

1 *School of Mechanical Engineering, Shandong University, Jinan 250061, China*
2 *Key Laboratory of High-efficiency and Clean Mechanical Manufacture (Shandong University), Ministry of Education, Jinan 250061, China*

Received June 25, 2014; revised November 24, 2014; accepted January 7, 2015

**Abstract:** The mechanical properties of ceramic cutting tool materials can be modified by introducing proper content of nanoparticles or whiskers. However, the process of adding whiskers or nanoparticles has the disadvantages of high cost and health hazard as well as the agglomeration; although a new in-situ two-step sintering process can solve the above problems to some extent, yet the problems of low conversion ratio of the raw materials and the abnormal grain growth exist in this process. In this paper, an in-situ one-step synthesis technology is proposed, which means the growth of whiskers or nanoparticles and the sintering of the compact can be accomplished by one time in furnace. A kind of Ti(C, N)-based ceramic cutting tool material synergistically toughened by $TiB_2$ particles and whiskers is fabricated with this new process. The phase compositions, relationships between microstructure and mechanical properties as well as the toughening mechanisms are analyzed by means of X-ray diffraction (XRD) and scanning electron microscopy (SEM). The composite which is sintered under a pressure of 32 MPa at a temperature of 1700℃ in vacuum holding for 60 min can get the optimal mechanical properties. Its flexural strength, fracture toughness and Vickers hardness are 540 MPa, 7.81 MPa • $m^{1/2}$ and 20.42 GPa, respectively. The composite has relatively high density, and the in-situ synthesized $TiB_2$ whiskers have good surface integrity, which is beneficial for the improvement of the fracture toughness. It is concluded that the main toughening mechanisms of the present composite are whiskers pulling-out and crack deflection induced by whiskers, crack bridging by whiskers/particles and multi-scale particles synergistically toughening. This study proposes an in-situ one-step synthesis technology which can be well used for fabricating particles and whiskers synergistically toughened ceramic tool materials.

**Keywords:** in-situ synthesis technology, $TiB_2$ whisker; toughening mechanism, Ti(C, N)-$TiB_2$ composite, tool material

## 1 Introduction

Ceramic cutting tool materials have great advantages in the field of high-speed machining compared to the traditional high-speed steel and cemented carbide cutting tools, due to the high hardness, excellent wear and corrosion resistance of ceramics as well as good chemical stability. However, the brittleness and poor damage tolerance have limited the wide application of ceramics. Up to now, several useful methods have been proposed in order to improve the fracture toughness and flexural strength of ceramic materials, such as micro/nano-scale particles strengthening and toughening method[1], whiskers/fibers/nanotubes or plate-like grains toughening method[2–5], phase transformation toughening process and self-toughening technology[6].

* Corresponding author. E-mail: lhl70@sdu.edu.cn
Supported by National Natural Science Foundation of China(Grant No. 51175305), Key Special Project of Numerical Control Machine Tool of China(Grant No. 2012ZX04003-051), and China Postdoctoral Science Special Foundation(Grant No. 2012T50610)


By separately adding nano-scale particles or whiskers with high strength and high elastic modulus into the ceramic matrix, the strength and toughness can be greatly improved[7–9], especially when adding whiskers the high temperature mechanical properties of ceramics can be higher[10]. The strengthening and toughening effects get remarkable with the increased content of reinforcing phase; however, when the content of nano-scale particles is high, the nano-particles tend to agglomerate, thus during the sintering process, the agglomerate particles grow fast and develop into large grains, and the fast moving grain boundaries lead to mass of pores entrapped into the grown grains, which results in poor densification and is harmful to mechanical properties[1]. Similarly, when the whisker content is higher, whiskers are hard to be dispersed, and it is easier to form three dimensional rigid network skeletons, this skeleton structure can produce bridging and springing effects during sintering, leading to the poor density and mechanical properties[11]. Compared with separately adding particles or whiskers, simultaneously adding both particles and whiskers can weaken the agglomeration phenomenon to some extent, thus the unique strengthening and toughening effects of nano-scale particles and whiskers can be well developed, and the mechanical properties of ceramic cutting tool materials can be improved[12–14]. But the process of adding whiskers or nanoparticles still has the disadvantages of high cost and health hazard because of the flexible preparation process of whiskers with small production[11, 15] In-situ synthesis technology can be used to directly fabricate reinforcing whiskers or particles in ceramic[2, 16] or metal matrix[17–19] and can be seen as an alternative strategy to overcome the above disadvantages. However, there are few reports about the in-situ synthesis of particles and whiskers toughened ceramic tool materials[20–22].

Although the in-situ two-step sintering process (i.e., first step for fabricating whiskers or nanoparticles in matrix and the second step for sintering the compact) [20–21] can solve the above problems to some extent, yet the problems of low conversion ratio of the raw materials and the abnormal grain growth exist in this process. In the present work, an in-situ one-step synthesis technology is proposed, which means the growth of whiskers or nanoparticles and the sintering of the compact can be accomplished by one time in furnace. With this process, an in-situ $TiB_2$ particle-whisker toughened Ti(C, N)-$TiB_2$ ceramic cutting tool material was fabricated. The morphology and toughening mechanisms of whiskers were discussed.

## 2 Experimental Procedures

### 2.1 Precursor materials and preparation procedures

Commercially available Ti, $B_4C$, BN and Ni powders were used as the precursor materials, of which Ni only acts as a sintering additive. The purity, particle size, manufacture and the main impurities of the precursor powders were shown in Table 1. The molar ratio of the precursor materials were listed in Table 2.

**Table 1. Purity, particle size, manufacture and impurity of the precursor materials**

| Substance | Purity wt.% | Particle size $d$/μm | Manufacture | Main impurity and comment wt.% |
|---|---|---|---|---|
| Ti | ~99.0 | ~48 | GRINM, China | CaO<0.05, MgO<0.05, $SiO_2$<0.01, $TiO_2$<0.005, $Fe_2O_3$<0.005 |
| BN | ~99.0 | ~1 | YPFC, China | $B_2O_3$>0.28, $N_3Na$>0.14, CaO>0.02, $Fe_2O_3$>0.05, $Al_2O_3$>0.006 |
| $B_4C$ | ~99.5 | ~1 | YPFC, China | Fe<0.05, Si<.05, C<0.5, O<0.3 |
| Ni | ~99.8 | ~48 | GRINM, China | Co<0.05, C<0.03, Fe<0.03, Pb<0.003, S<0.003, Mg<0.002 |

**Table 2. Mol ratio of the precursor materials**

| Samples No. | Mol ratio of the precursor materials $\alpha$/mol.% | | |
|---|---|---|---|
| | Ti | BN | $B_4C$ |
| TBCN | 2.9 | 0.7 | 0.3 |

The mixed slurries were ball-milled, and then dried in a vacuum dry-type evaporator (Moder ZK-82A, China). After that, the dried powders were sieved through a 100-mech sieve for further use. The dried powders were placed into a graphite die and in-situ hot-pressed with an applied pressure of 32 MPa at 1700℃ with the holding time of 60 min in vacuum in a sintering furnace.

### 2.2 Characterization

The sintered compacts were cut, ground and polished into specimens with a dimension of 3 mm×4 mm×30 mm. The flexural strength was tested using the three-point bending tester (Model WD-10, China) with a span of 20 mm and a loading velocity of 0.5 mm/min. The Vickers hardness was measured on the polished surface using a Vickers diamond pyramid indenter (Model 120, China) with a load of 196 N and a loading holding time of 15 s. The fracture toughness measurement of materials was determined by the Vickers indentation method proposed by EVANS, et al[23]. The relative density of specimens was measured by the Archimedes' method with the distilled water as medium. The fractured surfaces and cracks on the polished surfaces were observed by scanning electron microscopy (SEM, SUPRA-55, ZEISS, Germany). Phase identification was carried out by X-ray diffraction analysis (XRD, RAX-10A-X, Hitachi, Japan) with copper Kα radiation.

## 3 Results and Discussion

### 3.1 Phase composition and microstructure

Fig. 1 showed the XRD pattern of the sample. It revealed that $TiC_{0.3}N_{0.7}$ and $TiB_2$ were the major phases synthesized by reaction (1) in the sintering process, and there were no other intermediate phases or impurities.

$$(1+2x+0.5y)Ti + xB_4C+yBN=TiC_xN_y+ (2x+0.5y)\ TiB_2,\quad x+y=1, \tag{1}$$

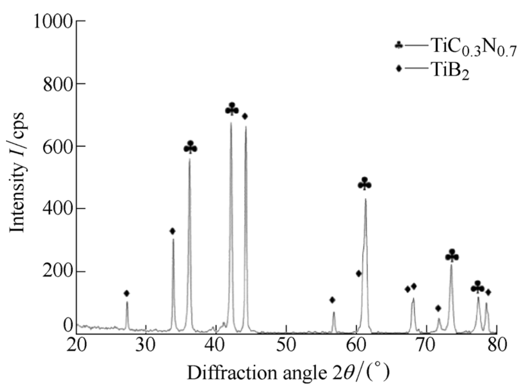
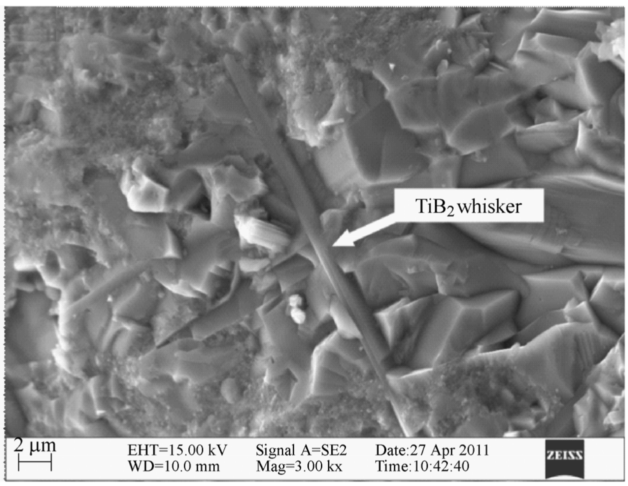
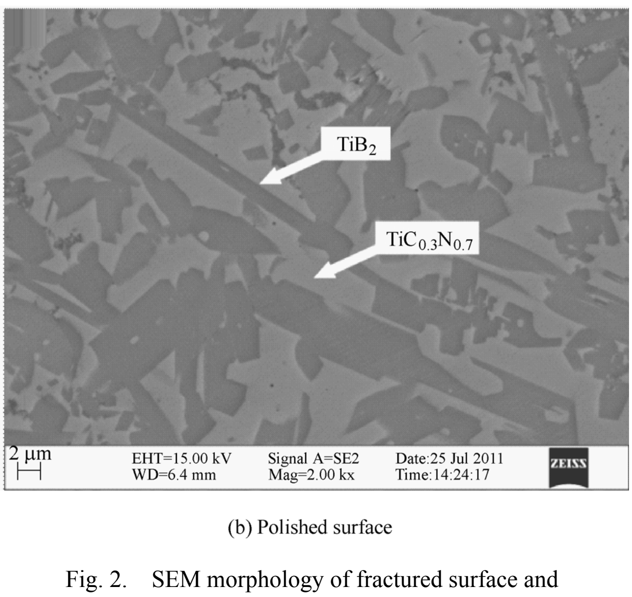



Fig. 1. XRD pattern of Ti(C,N)-$TiB_2$ ceramic tool material

The SEM morphology of fractured surface of the sintered composite was shown in Fig. 2(a). It revealed that the diameter, length and aspect ratio of $TiB_2$ whiskers were about 0.5−1 μm, 20 μm and 20, respectively. The $TiB_2$ whiskers synthesized by in-situ reaction had complete and clean surface, and the whisker section presented regular hexagon or quadrangle. Fig. 2(b) showed the SEM morphology of polished surface of the composite. The black phase was $TiB_2$ and the grey phase was $TiC_{0.3}N_{0.7}$. It was found that the whiskers are uniformly distributed among the matrix, and the pores were hardly observed on the polished surface, which indicated that the composite had high density. Therefore, the integrated fabrication process of whisker synthesis and composite densification was achieved by one step.




(a) Fractured surface




(b) Polished surface

Fig. 2. SEM morphology of fractured surface and polished surface of Ti(C, N)-$TiB_2$ composite

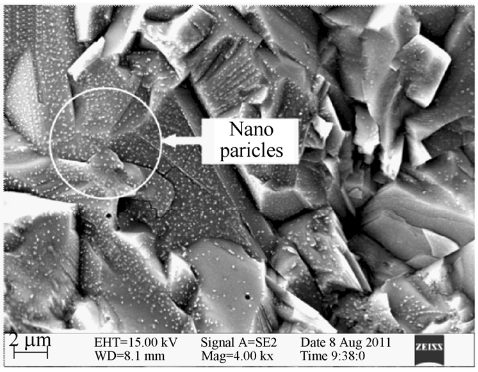
### 3.2 Mechanical properties and toughening mechanisms

The mechanical properties of the sintered composite ceramic tool material were shown in Table 3. The fracture toughness of the whisker-toughened composite synthesized by in-situ reaction was improved markedly. Due to the high elasticity modulus and high strength of $TiB_2$ whiskers, when the external load was applied on the material, the $TiB_2$ whiskers could well undertake and transfer the load, thus the flexural strength of the composite was enhanced. Additionally, instant high temperature induced by the exothermic reaction (1) promoted the densification, leading to the higher density, which is beneficial for the increase of flexural strength.

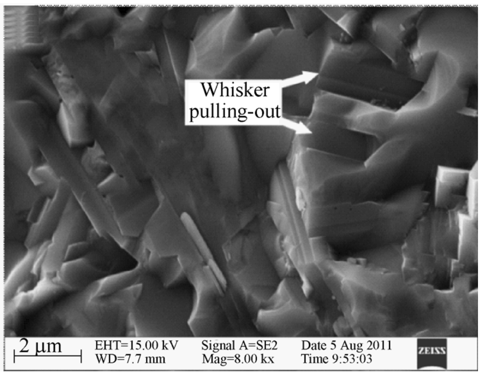
**Table 3. Mechanical properties of Ti(C, N)-$TiB_2$ composite ceramic tool material**

| Composite | Flexural strength $\sigma_f$/MPa | Vickers hardness $H_V$/GPa | Fracture toughness $K_{IC}$/(MPa • $m^{1/2}$) |
|---|---|---|---|
| Ti(C,N)-$TiB_2$ | 540 | 20.42 | 7.81 |

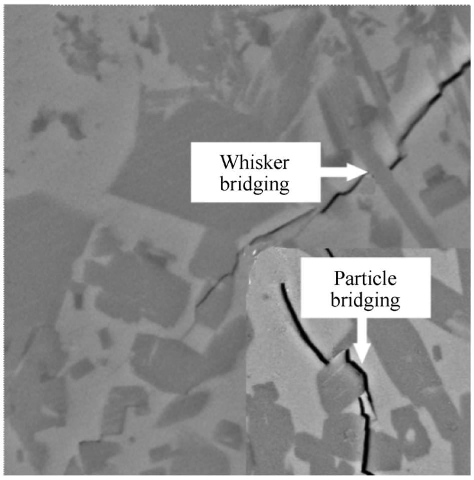
The fracture toughness of the composite was much higher than that of monolithic Ti(C, N) or $TiB_2$. The increased fracture toughness was ascribed to the synergistic toughening effects of the in-situ synthesized whiskers and particles. The main toughening mechanisms were analyzed combining with the SEM morphologies shown in Fig. 3(a) to Fig. 3(e). Firstly, the nano-scale phases formed from the in-situ reaction were uniformly distributed at the surfaces of whiskers and particles, which made the interfaces much coarser as shown in Fig. 3(a). Thus, it was believed that the coarse surface could enhance the frictional force when whiskers pulling-out from the matrix. Secondly, Fig. 3(b) showed the left holes after the whiskers pulling-out. Whisker pulling-out would consume much more fracture energy, so the fracture toughness would be promoted. Moreover, the effects of whiskers pulling-out could relax the stress of crack tip, and then the stress intensity factor of crack tip reduced. So, the effects of whisker pulling-out were beneficial for the increase of fracture toughness. Thirdly, cracks were bridged by a portion of $TiB_2$ whiskers and particles located at particular places as shown in Fig. 3(c) and Fig. 3(d). The crack bridging whiskers and particles connect two surfaces of a crack and provide with a force which makes two surfaces of a crack draw close. This results in the increase of stress strength factor of the composite with the extension of crack. Fourthly, Crack deflection was also observed in Fig. 3(e). Due to the high strength of $TiB_2$ whisker, when the cracks encounter $TiB_2$ whisker, the cracks tended to be deflected and propagated along the $TiB_2$ whisker. Thus the crack propagation path extended, which was beneficial for improving the toughness by the increased consumption of fracture energy. Moreover, the particle size ranging from nano-scale to micro-scale had the multi-scale synergistically strengthening and toughening effects.



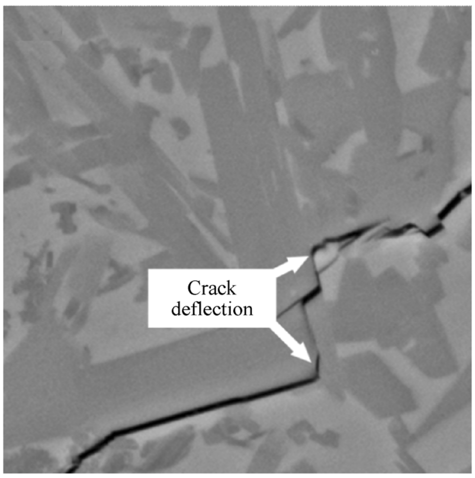

(a) Nano-scale particle toughening




(b) Whisker pulling-out




(c) Whisker bridging, (d) Particle bridging




(e) Crack deflection

Fig. 3. SEM morphology showing different toughening mechanisms

## 4 Conclusions

(1) A type of Ti(C, N)-based ceramic cutting tool material synergistically toughened by $TiB_2$ particles and whiskers was fabricated by in-situ synthesis technology, with this process the whisker synthesis and composite densification were carried out by one step. The composite had relatively high density, and the $TiB_2$ whiskers possessed good surface integrity.

(2) The fracture toughness of the new Ti(C, N)-$TiB_2$ composite was markedly improved up to 7.81 MPa • $m^{1/2}$. The flexural strength and Vickers hardness were 540 MPa and 20.42 GPa, respectively.

(3) The main toughening mechanisms of the present composite were crack bridging by whiskers and particles, whiskers pulling-out, crack deflection and multi-scale particles synergistically toughening.

**References**


[1] YIN Zengbin, HUANG Chuanzhen, ZOU Bin, et al. Preparation and characterization of $Al_2O_3$/TiC micro-nano-composite ceramic tool materials[J]. *Ceramics International*, 2013, 39(4): 4253−4262.

[2] ZHAO Guolong, HUANG Chuanzhen, LIU Hanlian, et al. A study on in situ growth of TaC whiskers in $Al_2O_3$ matrix powder for ceramic cutting tools[J]. *Materials Research Bulletin*, 2012, 47(8): 2027−2031.

[3] LIN Jia, ZHANG Xinghong, HAN Wenbo, et al. The hybrid effect of SiC whisker coupled with $ZrO_2$ fiber on microstructure and mechanical properties of $ZrB_2$-Based ceramics[J]. *Materials Science and Engineering: A*, 2012, 551: 187−191.

[4] WANG Weili, BI Jianqiang, SUN Kangning, et al. Fabrication of alumina ceramic reinforced with boron nitride nanotubes with improved mechanical properties[J]. *Journal of the American Ceramic Society*, 2011, 94(11): 3636−3640.

[5] HU Chunfeng, ZOU Ji, HUANG Qing, et al. Synthesis of plate-like $ZrB_2$ grains[J]. *Journal of the American Ceramic Society*, 2012, 95(1): 85−88.

[6] BECHER P F. Microstructural design of toughened ceramics[J]. *Journal of the American Ceramic Society*, 1991, 74(2): 255−269.

[7] CAO Mengran, WANG Shubin, HAN Wenbo. Influence of nano sized SiC particle on the fracture toughness of $ZrB_2$-based nanocomposite ceramic[J]. *Materials Science and Engineering A*, 2010, 527(12): 2925−2928.

[8] BECHER P F, WEI G C. Toughening behavior in SiC-whisker-reinforced alumina[J]. *Journal of the American Ceramic Society*, 1984, 67(12): 267−269.

[9] SILVESTRONI L, SCITI D, MELANDRI C, et al. Toughened $ZrB_2$-based ceramics through SiC whisker or SiC chopped fiber additions[J]. *Journal of the European Ceramic Society*, 2010, 30(11): 2155−2164.

[10] DENG Jianxian, AI Xing, ZHAO Jun. Study on high temperature mechanical properties of $Al_2O_3/TiB_2/SiC_w$ composites[J]. *Journal of Inorganic Materials*, 1996, 11(1): 63−68.

[11] WANG Qiuhong, ZHENG Yong, SUN Fan, et al. Preparation of SiC whisker and application in reinforce of composite materials[J]. *Cemented Carbide*, 2010, 27(1): 49−54. (in Chinese)

[12] LAN Junsi, DING Peidao, HUANG Nan. SiC whiskers and Ti(C, N) particles synergistically toughened $Al_2O_3$ matrix ceramic composites for cutters[J]. *Journal of Materials Science & Engineering*, 2004, 22(1): 59−64. (in Chinese)

[13] SUN Lihong, ZHU Qifang, WANG Ruikun, et al. Study on fracture behavior of $Si_3N_4$ base composite ceramics adding SiC

nano-powders and SiC whiskers[J]. *Chinese Journal of Rare Metals*, 2000, 24(5): 330−334. (in Chinese)

[14] WANG Hailong, WANG Changan, ZHANG Rui, et al. Properties of $ZrB_2$ ceramics reinforced by SiC nanowhiskers and SiC particles[J]. *Acta Materiae Compositae Sinica*, 2009, 26(4): 95−101. (in Chinese)

[15] LI Yawei, WANG Qinghu, FAN Haibing, et al. Synthesis of silicon carbide whiskers using reactive graphite as template[J]. *Ceramics International*, 2014, 40: 1481−1488.

[16] ZHAO Guolong, HUANG Chuanzhen, LIU Hanlian, et al. Microstructure and mechanical properties of $TiB_2$−SiC ceramic composites by reactive hot pressing[J]. *International Journal of Refractory Metals and Hard Materials*, 2014, 42: 36−41.

[17] YAN Zhiqiao, CHEN Feng, CAI Yixiang, et al. Microstructure and mechanical properties of in-situ synthesized TiB whiskers reinforced titanium matrix composites by high-velocity compaction[J]. *Powder Technology*, 2014, 267: 309−314.

[18] HUANG Lujun, YANG Fuyao, HU Haiting, et al. TiB whiskers reinforced high temperature titanium Ti60 alloy composites with novel network microstructure[J]. *Materials and Design*, 2013, 51: 421−426.

[19] HAO Xuhong, LIU Changming, PAN Dengliang. Microstructure and mechanical behavior of in situ primary Si/$Mg_2Si$ locally reinforced aluminum matrix composites piston by centrifugal casting[J]. *Chinese Journal of Mechanical Engineering*, 2011, 24(4): 656−660.

[20] LIU Bingqiang, HUANG Chuanzhen, GU Meilin, et al. In situ growth of $TiC_xN_{1-x}$ whiskers in $Al_2O_3$ matrix for ceramic cutting tools[J]. *Materials Chemistry and Physics*, 2009, 113(2−3): 613−615.

[21] LIU Bingqiang, HUANG Chuanzhen, LU Xinyu, et al. In situ growth of TiC whiskers in $Al_2O_3$ matrix for ceramic machine tools[J]. *Ceramics International*, 2007, 33(8): 1475−1480.

[22] XU Liang, HUANG Chuanzhen, LIU Hanlian, et al. Study on in-situ synthesis of $ZrB_2$ whiskers in $ZrB_2$−ZrC matrix powder for ceramic cutting tools[J]. *International Journal of Refractory Metals and Hard Materials*, 2013, 37: 98−105.

[23] EVANS A G, CHARLES E A. Fracture toughness determinations by indentation[J]. *Journal of the American Ceramic Society*, 1976, 59(7−8): 371−372.

## Biographical notes

LIU Hanlian, born in 1970, is currently a professor at *Shandong University, China*. She received her PhD degree from *Shandong University, China*, in 2005. Her research interests include new kind ceramic tools, structural ceramics, and machining techniques with high efficiency and high quality, and so on.
Tel: +86-531-88396913; E-mail: lhl70@sdu.edu.cn

SHI Qiang, born in 1986, is currently an engineer in *Taian Dongyue Heavy Industry Co., Ltd, China*. He received his master degree from *Shandong University, China*, in 2012
E-mail: sq_1027@126.com

HUANG Chuanzhen, is currently a professor at *Shandong University, China*. He received his PhD degree from *Shandong University of Technology, China.* His research interests include ceramic tool materials, precision machining and machining reliability, etc.
Tel: +86-531-88392058; E-mail: chuanzhenh@sdu.edu.cn

ZOU Bin, born in 1978, is currently an associate professor at *Shandong University, China*. He received his PhD degree from *Shandong University, China*, in 2006. His research interests include the advanced manufacturing technology, the machining techniques with high efficiency and high quality, and so on.
Tel: +86-531-88396912; E-mail: zb78@sdu.edu.cn

XU Liang, born in 1984, is currently an engineer at *Aerospace Research Institute of Materials & Processing Technology, China.* He received his PhD degree from *Shandong University, China*, in 2013. His research interests include machining techniques with high quality and low damage, ceramic tools and fiber reinforced materials.
Tel: +86-10-68320044; E-mail: sduxlg@126.com

WANG Jun, born in 1960, is currently a professor at *University of New South Wales, Australia* with a conjoint appointment in *Shandong University, China* and several other universities. He obtained his PhD degree from *University of Melbourne, Australia*, in 1993. His main research interest is in advanced manufacturing technologies, in particular, traditional and non-traditional material removal processes.
E-mail: jun.wang@unsw.edu.au