Advanced Ceramic Dies: Design, Fabrication and Performance

(先进陶瓷模具：设计、制造与性能)

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内 容 简 介

本书是作者结合多年从事陶瓷模具研究的相关成果撰写而成。在全面综述国内外陶瓷模具及相关研究进展的基础上，主要介绍了先进陶瓷模具设计技术、制造工艺与性能研究的最新进展。书中首先阐述了计算智能技术如BP神经网络、遗传算法、免疫算法及其混合算法等在陶瓷模具材料组分与制备工艺优化设计方面的应用，并将有限元方法用于陶瓷模具结构优化设计，对冷热挤压模具及其挤压过程的热应力进行了计算与分析；基于设计结果，研制了氧化铝基、氧化锆基和碳氮化钛基微纳复合陶瓷模具材料，并详细介绍了其力学性能、微观结构与增韧补强机理；考虑到实际应用的需要，又进一步介绍了所研制的三种微纳复合陶瓷模具材料的摩擦与磨损特性。本书既有陶瓷模具材料与结构设计方面的理论分析与模拟计算，又有材料性能与摩擦磨损应用，反映了陶瓷模具领域近期的研究成果。

本书可供普通高等学校机械类、材料类专业研究生和高年级本科生阅读，也可供机械工程、材料加工工程、模具材料、模具设计与制造等相关领域的研究人员、工程技术人员参考。

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Preface

Die is one of the important equipment needed in modern industry. At present, die materials are mainly varieties of die steels and cemented carbides. Researches on ceramic dies have been greatly developed abroad, and many patents have been approved in Japan, America, France, etc. However, the corresponding research work is still being at the start stage in China. Although both theoretical and practical researches have been carried out, results are not entirely desired. In fact, because of its high hardness, high thermal resistance, and so on, wear resistance of ceramic materials is higher than that of high-speed steel and cemented carbides, and thus it can be used as die material. But ceramics is the brittle material which can't withstand high tensile stress. So, more attention should be paid to the properties of ceramics in the design, manufacture and application of dies so as to improve the reliability and chemical stability of ceramic dies. Research on the ceramic die needs to be further strengthened and deepened no matter in kind, property and application field.

The book is specially designed to introduce the recent advances in the field of advanced ceramic dies, including design technology, fabrication process and performances. After the brief introduction to ceramic die materials and ceramic die, the computational intelligence methods such as BP algorithm, immune algorithm, and hybrid IGA method, etc. are used for the optimum material design of the compositions and processing parameters. Then, the finite element method is employed to design optimally the die structure, with thermal stress analysis of cold and hot extrusion die and hot extrusion process. Al_2O_3 based, ZrO_2 based and Ti(C,N) based nano-micro composite ceramic die materials have been prepared with detailed analyses of mechanical property, microstructure, toughening and strengthening mechanisms. In order for the application, friction and wear behaviors of these three kinds of nano-micro composite ceramic die materials are further studied.

The subject area of the book mainly concerns about material forming and processing, especially that of die and mold, including the material design, structural design, material fabrication, microstructure, mechanical property, friction and wear behaviors.

The authors have devoted about ten years in the development and application of ce-

ramic die and molds. Under the support of the National Natural Science Foundation of China (50405047), the Natural Science Foundation of Shandong Province (Y2005F04), Research Fund for Excellent Young and Middle-aged Scientists of Shandong Province (2000-49, 2007BS04019), Science and Technology Development Plan of Educational Department of Shandong Province (J08LA18), Science and Technology Development Plan of Shandong Province (2009GG10004023) and Jinan Young Star Plan of Science and Technology (08108), series of research results related to the ceramic dies have been achieved. The book is written on the basis of these researches, and main contents are from the published papers and academic degree thesis of postgraduate students supervised by Professor Xu Chonghai. The aim of the book is to introduce the recent advances in the field of ceramic dies and to promote further the development and application of ceramic dies.

The book is written by Xu Chonghai, Xiao Guangchun, Zhang Jingjie and Yi Mingdong, Qilu University of Technology, and is compiled and edited finally by Xu Chonghai. Postgraduate students Zhao Shikui, Wang Xinghai, Jiang Zhenyu and Zhang Huifa are appreciated for their research work. Doctoral student Chen Zhaoqiang, postgraduate students Ma Jun and Meng Xianglong are appreciated for their helpful work in parts of writing and editing. The authors would like to thank Science Press for their warmly supports and help during the edition and publication.

Limited to the level of the authors, the book will inevitably have shortcomings. We would like to welcome criticism and suggestions from readers.

Xu Chonghai
July, 2015

Contents

Chapter 1
State of the Art of Ceramic Dies

1.1 Introduction

Die is one of the important equipment needed in modern industry. At present, die materials are mainly varieties of die steels and cemented carbides (Cui, 2001). Although the strength of die steels is high, its hardness is low and wear resistance is poor, so the service life of steel dies is shorter. From the 1980s, cemented carbides have been widely used as die materials with its better mechanical properties and wear resistance. As a result, its service life has also been increased greatly. With the rapid development of production, however, the high temperature strength and wear resistance of cemented carbides already can't satisfy the requirement of actual production. Therefore, it is urgently needed to develop a new generation of die materials which will have higher room-temperature and high-temperature strength, higher toughness and superior wear resistance.

Researches on ceramic dies have been greatly developed abroad, and many patents have been approved in Japan, America, France, etc (DeZuba, 1977; Ohuchi, 1991). However, the corresponding research work is still being at the start stage in China. Although both theoretical and practical researches have been carried out (Luo, 2002; Xu, 1996), results are not entirely desired. In fact, because of its high hardness, high thermal resistance, and so on, wear resistance of ceramic materials is higher than that of high-speed steel and cemented carbides, and thus it can be used as die material. But ceramics is the brittle material which can't withstand high tensile stress. So, more attention should be paid to the properties of ceramics in the design, manufacture and application of dies so as to improve the reliability and chemical stability of ceramic dies. Research on the ceramic die needs to be further strengthened and deepened no matter in kind, property and application field. In the present study, research status quo of design, fabrication, property and application of ceramic dies are comprehensively summarized and the perspectives in the application of ceramic dies are also pointed out.

1.2 Composition, processing technology and mechanical property of ceramic die materials

1.2.1 Al_2O_3 based ceramics

1.2.1.1 ZTA

ZrO_2 toughened Al_2O_3 based composite ceramic (ZTA) can be used to fabricate wire drawing dies (Xu, 1996) and inner circles of extrusion combined female die (Liu, 1997). As one of new die materials, some of its properties are higher than that of high speed steel and cemented carbides. Y-ZTA superfine composite powders were prepared with $(NH_4)Al(SO_4)_2 \cdot 12H_2O$, $ZrOCl_2 \cdot 8H_2O$ and Y_2O_3 raw materials with chemical liquid-phase method. Y-ZTA ceramics of different compositions were then fabricated with hot pressing technique. By controlling Y_2O_3 content in Y-PSZ and Y-PSZ content in ZTA, ZrO_2 in matrix can exist to the maximum extent in the form of metastable tetragonal phase. The optimum conditions are 4wt% Y_2O_3 and 18wt% Y-PSZ. The fracture toughness and flexural strength of ZTA ceramic are all increased simultaneously to be approximately 7.2MPa·$m^{1/2}$ and 740MPa, respectively (Table 1.1).

Table 1.1 Properties of the ceramic die materials

Die materials	Flexural strength /MPa	Fracture toughness /(MPa·$m^{1/2}$)	Hardness /GPa	Coefficient of thermal expansion /(10^{-6}℃$^{-1}$)
ZTA	740	7.2	18	–
TZP/TiC/Al_2O_3	1106	11.86	–	–
TZP	1335	10	15	–
3Y-TZP	1052	36.4##	90.5*	–
ZrO_2 (PS)	1120	–	–	8.3
Z-MAT 250	2000	8	13	10
2016	210	6	5.9	7.3**
5027	350	7.2	7.46	2.4
(Ce-TZP)-Al_2O_3	892	14.3	10.9	–
(3Y-TZP)-Al_2O_3	1450–1490	10.5–11	15–16.5	–
PSZ	650–850	10–14	>90*	–
PSZ (HP)	1400	5.5	13.0	11.5
Sialon	682(814#)	9.55	91.5*	4.01

Note: PS–pressureless sintering; HP–hot pressing.

* means unit is HRA; ** indicates value from room temperature to 600℃; # means value at 1000℃; ## means impact toughness.

1.2.1.2 TZP-TiC-Al_2O_3

The corresponding TZP-TiC-Al_2O_3 ceramic die material was prepared by hot pressing technique with the mixture of Al_2O_3 matrix, 25vol% TiC dispersed phase and 15vol%–30vol% TZP. It indicates that (Yin, 1997) the incorporation of TZP and TiC can prominently improve the mechanical property of Al_2O_3 ceramic. The flexural strength and fracture toughness was improved to be 1106MPa and 11.86MPa·$m^{1/2}$, respectively (Table 1.1).

When TZP-TiC-Al_2O_3 ceramic was used to make die, cold stamping dies and mould cores were made of the 45# steel. The samples were then formed by cold pressing and sintering of the ceramic powders. Ceramic die blanks and holes were processed by finishing. After inlaid processing, the ceramic dies were used to draw screw wires with the lubrication of lubricating powders and mechanical lubricating oil (30#). It was shown that (Yin, 1997) when the content of TiC is constant, wear resistance and fracture resistance of dies are obviously improved with the increase of TZP content (Fig. 1.1). When the content of TZP is increased from 15% to 25%, the wear amount is almost decreased one times. It is believed that the possible toughening mechanisms are stress induced TZP phase transformation, crack deflection and bridging, residual stress, and so on. The improvement in the mechanical property results directly in the improvement of wear resistance and fracture resistance of die materials.

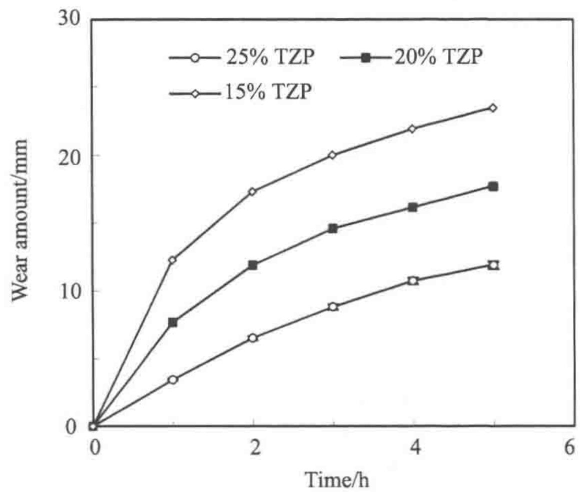

Fig. 1.1 Variation of wear amount of ceramic dies of different TZP contents with time (Yin, 1997)

1.2.2 ZrO_2 based ceramics

1.2.2.1 TZP

According to the working condition of wire drawing dies, 3Y-8Ce-TZP (addition of small amount of Al_2O_3) ceramic powders with the diameter of 0.49μm were prepared with $ZrOCl_2 \cdot 8H_2O$, Y_2O_3, CeO_2 and $AlCl_3 \cdot 7H_2O$ raw materials by the co-precipitation method. The powders were firstly pressed into samples and then put into the electric furnace sintering pressurelessly under atmosphere. The technological condition was that the heating rate was 3–5℃/min under 800℃, 2–3℃/min at 800–1000℃, 1–2℃/min at 1000–1450℃ and the tapping temperature was less than 200℃. The fracture toughness, flexural strength and hardness of the developed wire drawing die material is $10MPa \cdot m^{1/2}$, 1335MPa and 15GPa, respectively (Table 1.1) (Yang, 2001). It was found from drawing experiments that the developed TZP wire drawing dies can work continuously for an average time of 22.2h when used to draw H08JMn2SiA welding wires at a drawing speed of 3.5–4.5m/s. The average die life is 2.05 times longer than that of YG8 cemented carbide wire drawing dies.

Working as an important but easily-consumed part of the automatic rotary press machine, blanking dies have got widespread application in various industry fields. But because of the high cost of both 3Y-TZP ceramic raw material and the machining of dies, the cost seems to be too high in the manufacturing of the integral ceramic die. In order to save the cost and improve the performance-price ratio, the working surfaces of die can be manufactured with 3Y-TZP ceramics, while the non-working surfaces can be fabricated by steels according to the working condition and the stress state of blanking dies. Then, after two parts are bonded together, high performance dies with high wear resistance, high impact resistance and reasonable cost can eventually be achieved (Hu, 2002).

The specific preparation technology is following (Hu, 2002). 3Y-TZP micro powders were adopted with the average size of 0.4μm. 3Y-TZP nanometer powders were also prepared by the co-precipitation method and its average size is 20nm. Blanking die material is composed of 3Y-TZP micro powders working as matrix phase and 3%–10% 3Y-TZP nanometer powders. The powders were fast milled in planet ball milling machine for 1h with the dispersing media of alcohol and milling media of 3Y-TZP balls and then dried in the drying oven for reservation. The samples were fabricated through isostatic pressing (250MPa) and sintering (1460℃ for 2h). Thus, high performance composite 3Y-TZP ceramic die material was manufactured through the incorporation of small amount of 3Y-TZP nano-powders into the corresponding micro powders. The addition of 3Y-TZP nano-powders can remarkably enhance the strength and hardness of TZP ceramic die material by means of the transformation toughening of ZrO_2 and toughening and reinforcing by nano powders. It also can decrease the sintering temperature from 1540℃ to 1480℃.

In addition, ceramic materials such as pressurelessly sintered ZrO_2 used as isothermal wire drawing dies (Huang, 1991) and ZrO_2 ceramic material as extrusion dies (Gu,

1989) have been studied from 1990s. Mechanical properties of the material are listed in Table 1.1. Good results have also been achieved abroad in the application of Y-TZP ceramic dies such as Z-MAT 250 produced in Norton Advanced Ceramics Company. Its fracture toughness, flexural strength and hardness is $8MPa{\cdot}m^{1/2}$, 2000MPa and 13GPa, respectively (Cris, 2000). 2016 and 5027 die materials, produced in Zircoa Company, is mainly composed of ZrO_2 (96.5%) with additional 3.1wt%–3.3wt% MgO and small amount of rare earth additives. Its fracture toughness is $6–7.2MPa{\cdot}m^{1/2}$ and the Weibull modulus reaches 14.

1.2.2.2 (Ce-TZP)-Al_2O_3

In consideration of the requirements of high toughness in the manufacture and application of dies, Liu et al. (1996; 2003) chose (Ce-TZP)-Al_2O_3 composite ceramic as hot extrusion die material. Because of its large critical particle size, good processing properties and no obvious low temperature deterioration phenomenon, Ce-TZP exhibits good strength and toughness under the phase transformation temperature 1170℃ of ZrO_2. It can satisfy the temperature requirement of the hot extrusion of copper and aluminum. However, the hardness of single phase Ce-TZP material is low and the wear resistance is insufficient. A certain amount of Al_2O_3 particles of high hardness were incorporated into the ZrO_2 matrix in order to improve the mechanical property and wear resistance of the composite.

CeO_2-ZrO_2-Al_2O_3 composite powders were prepared with co-precipitation coating method and the compositions is 10mol% CeO_2-ZrO_2-(15wt%–20wt%) Al_2O_3 (Liu et al., 1996; 2003). The processing technology includes dry press forming, cold isostatic pressing, pre-sintering, machining, high temperature sintering and grinding. The pressure in dry press forming is 100–150MPa, pressure in cold iso-static pressing is 200–300MPa, pre-sintering temperature is 1000–1200℃ and high temperature sintering temperature is 1550–1650℃. Properties of the developed (Ce-TZP)-Al_2O_3 ceramic die material are that flexural strength is 892MPa, fracture toughness is $14.3MPa{\cdot}m^{1/2}$, relative density is higher than 99%, Vickers hardness is 10.9GPa and permissible working temperature is 650℃ (Table 1.1).

1.2.2.3 3Y-TZP/Al_2O_3

The ceramic material 3Y-TZP-Al_2O_3 had also been developed successfully to manufacture drawing dies (Luo, 2002). The powders were prepared with co-precipitation method and composed of $ZrO_2Cl_2{\cdot}8H_2O$, Y_2O_3, $AlCl_3{\cdot}6H_2O$ and $NH_3{\cdot}H_2O$. The ingredient was prepared with the addition of 3mol%Y_2O_3 and small amount of Al_2O_3 with dispersant and complexing compound and neutralized with $NH_3{\cdot}H_2O$. After washing, filtering, dewatering, calcinations, ball milling and drying, the powder diameter is 40nm. Samples were than fabricated by cold pressing method under 120MPa for 3min and then sintering at 1450℃ for 4h. The material has high strength, high hardness and high toughness. Especially, its fracture toughness is more than 10MPa·m$^{1/2}$ because of the dominant toughening effect of ZrO_2. On the other hand, Al_2O_3 was used as the second phase to noticeably increase the room temperature and high temperature mechanical properties, the anti-aging ability at low temperature and the sintering ability of the composite. As a result, its flexural strength researches 1450–1490MPa and hardness is 15–16.5GPa, which can completely satisfy the requirements of drawing dies (Table 1.1).

1.2.2.4 PSZ

PSZ ceramic is one of the most promising hot extrusion die materials (Gulati, 1980). Superfine PSZ powders were produced by the co-precipitation method with the purity higher than 99% and the average particle size of 0.4–0.6μm. The hot extrusion dies were then formed by the pre-pressing, pressing and forming, pressureless sintering, grinding and subsequent inlaid processing. Its fracture toughness, flexural strength and hardness is 10–14MPa·m$^{1/2}$, 650–850MPa and 90HRA, respectively (Table 1.1) (Shen, 1996).

In addition, ceramic material of PSZ used as blanking dies had been studied in the early 1990s (Aoki, 1990). The mechanical properties of the material are given in Table 1.1.

1.2.3 Sialon ceramics

Since the working temperature of hot extrusion dies is high (variation between 600℃ and 1200℃ according to different extrusion materials) and at the same time it must bear high tensile stress, β'-Sialon ceramics that has good high temperature mechanical properties can be expected in the fabrication of hot extrusion dies. The typical composition of β'-Sialon is 75%–88% Si_3N_4, 4%–6% AlN, 6%–10% Y_2O_3 and small amount of Al_2O_3 and La_2O_3 additives. The die material was formed by the mould pressing with the pressure of 1000MPa, cold isostatic pressuring with the pressure of 250MPa and pressureless sintering process. The material was sintered at 1750℃ in the nitrogen atmosphere. Its fracture toughness and flexural strength amounts to 9.55MPa·m$^{1/2}$ and 682MPa, respectively and the flexural strength even reaches 814MPa at 1000℃ (Table 1.1) (Liu, 2003; 1995).

β'-Sialon ceramic hot extrusion die was compared with 3Cr2W8V alloyed steel hot extrusion die used in production. It indicated that (Liu, 1995) ceramic hot extrusion dies have obvious superiority. But for the alloy steel dies of 3Cr2W8V, plastic flow phenomenon appeared under working temperature. Higher adhesion tendency with the brass material occurred which is easy to result in the blocking phenomenon. Then, it will cause products over tolerance and high surface roughness.

Compared with the extrusion dies of Ce-TZP ceramic, although its room temperature strength and fracture toughness are lower, the high temperature property of β'-Sialon hot extrusion ceramic die is better. Furthermore, plasticity of the copper is improved at high temperature. As a result, the extrusion pressure is reduced and the stress state is correspondingly changed at high temperature. For Ce-TZP ceramic extrusion dies, however, the working temperature can not be too high because the strength and toughness of the material will noticeably be decreased above the phase transformation temperature of ZrO_2 and the friction stress can also accelerate the phase transformation process. On the other hand, low extrusion temperature can cause the extrusion pressure to be increased. It is also one of the reasons why the life of Ce-TZP extrusion die is lower than that of β'-Sialon extrusion die.

The hardness of Sialon ceramic material used as iso-thermal forging dies is about 11–14GPa at 200–1600℃ (Kiyoyuki, 1991), the flexural strength is about 840MPa at room temperature and it still can reach 700MPa at 1600℃. Furthermore, the coefficient of thermal expansion is very low. Therefore, it can satisfy well the requirements of engineering performances of dies.

1.2.4 Si_3N_4 ceramics

Si_3N_4 ceramics, particularly the reaction sintered Si_3N_4 ceramics, have good mechanical properties, wear resistance, thermal shock resistance and chemical stability. They can be conveniently made into varieties of parts even with complex shape. Therefore, Si_3N_4 ceramic materials can work as a sort of potential die materials. Liang et al. (2000) took silicon powders of 100 mesh to be pressed into blanks with the hydraulic machine (model YA-100) and then iso-static pressed under 300MPa. After rough machining, bodies were then sintered pressurelessly in an N_2 atmosphere at 1450℃ in a 50kW electric furnace. The flexural strength and hardness of the prepared ceramic die material amounts to 200MPa and 82–87HRC, respectively. Its coefficient of friction is 0.05 and the thermal coefficient of expansion is $(2.5–3.0)\times10^{-6}℃^{-1}$.

1.2.5 Cermets

Cermets are also one type of good die materials. Zhou et al. (1987; 2002) had developed a series of cermet die materials. They are mainly composed of the matrix phase Mo or W, ceramic phase and other metal elements or rare earth oxides. Because the ceramic phases have excellent chemical stability and wear resistance, its hardness doesn't change obviously no matter at high temperature or at room temperature and it can form solid solution with metal elements, it can increase the thermal shock resistance and high temperature strength of materials. The material can be used to make hot extrusion dies or hot tamping dies of metal. The typical chemical composition includes 10wt%–60wt% W, 38.5wt%–80wt% Cr, 1wt%–30wt% Al_2O_3, 0–15wt% La_2O_3 and