

DOI: 10.11883/bzycj-2019-0395

Synthesis of nanometer titanium carbide by detonation shock wave*

YU Yanwu, JIA Kanghui, WEI Zihui, RU Ruifeng

(School of Environmental and Safety Engineering, North University of China, Taiyuan, Shanxi 030051, China)

Abstract: Nano titanium carbide (TiC) powder was synthesized by detonation shock utilizing octogen (HMX) as high temperature and high pressure source with titanium dioxide (TiO₂) and activated carbon (C) as precursors. The samples were characterized by X-ray diffraction (XRD), energy dispersive spectrometer (EDS) and scanning electron microscope (SEM). At the same time, detonation shock synthesis mechanism of nanometer TiC was discussed in this paper. It was concluded that the test results of XRD and EDS were in good agreement with the theoretical values, and the sample contained both TiC and TiC_x ($x < 1$). The particle size of both TiC and TiC_x ($x < 1$) were less than 50 nm by SEM photos and micron-sized spherical agglomerates were found in the samples. The detonation shock synthesis of TiC belongs to a special solid-phase reaction, and its material diffusion rate and reaction rate are greatly improved.

Keywords: synthesis; detonation shock; TiC; nanometer

爆炸冲击合成纳米碳化钛的研究

于雁武, 贾康辉, 魏子辉, 茹锐锋

(中北大学环境与安全工程学院, 山西 太原 030051)

摘要: 本文利用奥克托今炸药(HMX)作为高温、高压源, 二氧化钛(TiO₂)和活性炭(C)作为前驱体, 采用爆炸冲击合成的方法制备纳米碳化钛(TiC)粉末。运用X射线衍射分析仪(XRD)、X射线能谱分析仪(EDS)及扫描电子显微镜(SEM)对样品进行了分析与表征。探讨了爆炸冲击波作用下TiC的合成机理。结果表明: XRD和EDS测试值与理论值相符性很好, 样品中同时含有TiC和TiC_x($x < 1$); SEM照片显示TiC和TiC_x($x < 1$)的粒径均小于50 nm, 样品中存在微米级的球形团聚体; 爆炸冲击合成TiC属于特殊的固相反应, 其物质扩散速度和反应速度大大提高。

关键词: 合成; 爆炸冲击; TiC; 纳米

中图分类号: O389; O521.3

国标学科代码: 13035

文献标志码: A

Titanium carbide (TiC) is a typical transition metal carbide characterized by its high elastic modulus, low coefficient of thermal expansion, remarkable high-temperature strength, and superior resistance to abrasion and oxidation^[1]. It is widely used in structural materials for cutting tools, abrasion resistance coatings, mechanical parts and other fields. In addition, transparent ceramics TiC can also be used as excellent optical materials. TiC has excellent thermal shock resistance, which is often used as a special refractory in reductive or neutral atmospheres. TiC based cermets possess high hardness, high strength, oxidation resistance, high temperature resistance and chemical stability, as well as good toughness^[2]. As an excellent material, TiC has attracted wide attention all over the world and many researchers have used different methods to synthesize it. These methods mainly include carbothermal reduction method^[3-5], direct synthesis method^[6-7], sol-gel method^[8], gas phase method^[9-10], mechanic-

* Received date: 2019-10-16; Revised date: 2019-12-16

Fundation item: Open cooperative innovation project of Xi'an modern chemistry research institute (20190387)

Biography: YU Yanwu (1977-), male, Ph.D., associate professor, 815274820@qq.com

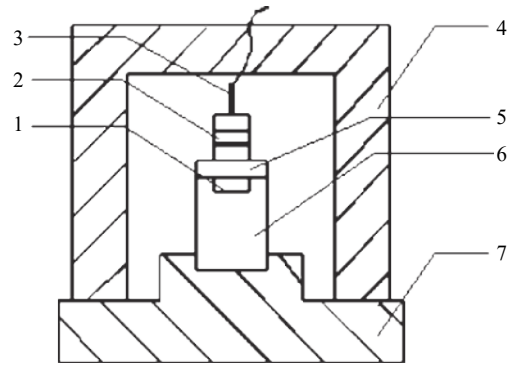
al alloy^[11], etc. In view of the fact that the research has not been carried out at home and abroad on the synthesis of titanium carbide by precursors directly driven by detonation shock of explosives, and it's only reported that the synthesis of titanium carbide may require a high temperature and high pressure condition. So the detonation shock method is used to synthesize TiC in this paper.

The detonation shock synthesis is a new field of science and technology rising in recent years, and the instantaneous high temperature and high pressure condition provided by detonation shock process can make the properties of materials change complicatedly. At present, the detonation shock method has been applied to powder processing, synthesis of super-hard materials, sinter and weld of new materials, and other fields. In this paper, nanometer TiC powder was synthesized by detonation shock wave. The structure, morphological characterization and elemental composition of the as-prepared samples were analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy dispersive spectrometer (EDS), respectively.

1 Experimental

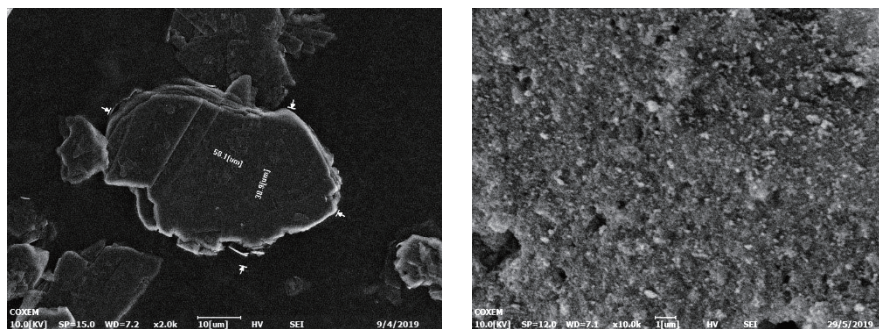
The schematic diagram of the experiment in a closed detonation reactor designed by our team is shown in Fig.1. HMX was selected as the pressure and temperature source. Detonation shock wave was adjusted by polymethylmethacrylate (PMMA, density 1.18 g/cm³). The precursors are TiO₂ and activated carbon. The HMX and the precursors were respectively pressed into a cylinder with a diameter of 10 mm and a height of 5 mm. The density of HMX cylinder and the precursor cylinder are 1.8 and 1.5 g/cm³, respectively. By the end of detonation shock wave, black powder products were obtained, accompanied by the release of ammonia gas. The black powder turned brown after being soaked in aqua regia for 24 hours, then it was calcined in muffle furnace for 400 min at 400 °C. Ultimately, the light grey powder was obtained.

Fig.2 shows the SEM diagram of the raw material. In the Fig.2(a), the activated carbon has a large layer and a flat surface. It has a obvious delamination and the edge is defective but not very large. Fig.2(b) shows that the particle size of titanium dioxide is very small.



1. precucers; 2. HMX; 3. electric detonator; 4. reaction vessel; 5. methylmethacrylate; 6. steel sleeve; 7. bed plate

Fig. 1 Experimental device



(a) Activated carbon

(b) Titanium dioxide

Fig. 2 SEM images of raw material

In order to improve the pressing formability of HMX cylinder, the water suspension granulation method was used to coat HMX with fluoro rubber 2602 whose mass fraction is 3% as a binder. The shock pressure required for the experiment is theoretically calculated according to the attenuation model of detonation shock wave^[12], which considers that the detonation shock wave decays exponentially during the propagation in the medium, and the attenuation relationship can be expressed by the following formula

$$p = ke^{-ax} \quad (1)$$

where p is the output pressure after attenuation, k is the correction factor, which is related to the density of HMX, a is the parameter of organic glass material, and x is the thickness of PMMA plate.

The XRD instrument used in the experiment is the D/MAX-rBX ray diffractometer by Japanese Science. The test was processed by using the standard $\theta-2\theta$ scanning method. The copper target $K\alpha_1$ radiation ($\lambda=1.54056 \times 10^{-10}$ m) was projected onto the powder. For each measurement, the machine was operated at 80 keV with a current of 100 mA, the scanning range is $20^\circ-100^\circ$ and the scanning rate is $4^\circ/\text{min}$. The SEM instrument used in the experiment was Tecnai G2 F20 S-TWIN type of FEI Company of the United States.

2 Result and conclusion

2.1 Analysis of structure

Fig.3 is the XRD curve of the sample produced by the detonation shock wave in the pressure of 25 GPa. The mole ratio of the reaction precursor TiO_2 and activated carbon is 1 : 6. There appeared 13 distinct peaks among which the Numbers 3, 4, 8 and 12 correspond to the crystal surface (111), (200), (220) and (400), respectively. The Numbers 5, 9, 10 are the peaks of TiC_x ($x < 1$), and the Numbers 1, 2, 6, 7, 11 and 13 are the ones of TiO_2 .

It is seen in Fig.3 that under the instantaneous high temperature and high pressure provided by detonation shock wave, C in activated carbon was used

as a reducing agent to reduce TiO_2 to obtain crystalline TiC and TiC_x ($x < 1$), and a few unreacted TiO_2 were found in the samples. Sen^[13] used thermodynamic methods to determine the possibility of using carbothermic method to obtain TiC by calculating the relationship between the reaction enthalpy and temperature of C and TiO_2 , and the relationship between the Gibbs free energy of the reaction and the temperature and pressure. In addition, according to the C-Ti binary equilibrium phase diagram, it is known that TiC is non-stoichiometric, and the range of the atomic ratio of C to Ti is from 0.49 to 1.0 with the continuous change of reaction conditions, which explains the existence of TiC_x ($x < 1$) in the sample. In Fig.3, the TiC characteristic peak deviates from the standard value, which is mainly due to the formation of lattice defects caused by the instantaneous high temperature and high pressure. Besides, the molar ratio of C and TiO_2 also has some effect on the deviation of the characteristic peaks, which is consistent with the references^[13-14]. There is no peak of C in its elemental form due to the oxidation of partial C into CO gas. The remaining activated carbon is soaked in aqua regia and calcined at high temperature for 31 hours during the purification process, and is released in the form of gaseous CO_2 . TiO_2 is not completely removed in the purification process because of its stable physical and chemical properties and remains in the sample ultimately.

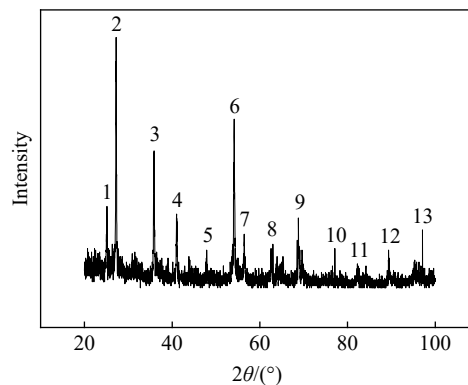


Fig. 3 XRD patterns of the prepared titanium carbide

2.2 Characterization of sample

Fig.4 is the SEM images of the samples. In Fig.4(a), there are particles distributed evenly with a size less than 50 nm. It shows that a small number of micron-sized spherical aggregates are attached to the nano-particles and band-shaped substances in Fig.4(b). The band-shaped substances should be residual of anatase TiO₂ according to the reference [15].

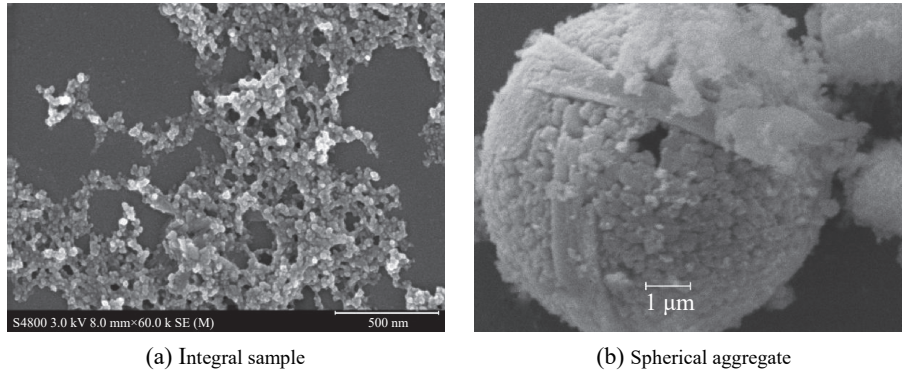


Fig. 4 SEM images of the samples

Table 1 and Table 2 show the results of the EDS spectrum of the samples. It is showed that four elements of Si, O, Al and Fe appears, besides C and Ti. According to the XRD results, TiC, TiC_x ($x < 1$) and TiO₂ were found in the samples. The element Si is derived from the organic glass filler, the sheath of detonator's lead and the adhesive tape during the experiment. Under the instantaneous high temperature and high pressure of the detonation shock, element Si is oxidized rapidly to amorphous SiO₂, which is consistent with the reference^[16]. A small amount of metallic elements in the sample mainly came from the detonator and inner debris of reactor vessel. These metallic elements produced stable metallic silicates in the sample during the experiment. It can be concluded from Table 2 that the composition of spherical aggregates is complex, which may be due to the co-agglomeration of TiC, TiC_x ($x < 1$), amorphous SiO₂, TiO₂ and metallic silicates, and the mechanism of agglomeration needs to be explored further.

Table 1 EDS spectrum of integral sample

Element	Line	Weight/%
C	K	23.36
O	K	12.51
Al	K	1.67
Si	K	18.87
Ti	K	42.20
Fe	K	1.39
Total		100.00

Table 2 EDS spectrum of Spherical aggregate

Element	Line	Weight/%
C	K	28.14
O	K	22.87
Al	K	2.11
Si	K	6.91
Ti	K	36.33
Fe	K	3.64
Total		100.00

2.3 Analysis of mechanism

In the traditional carbothermic method to synthesis titanium carbide, the order of forming product is Ti₄O₇, Ti₃O₅, Ti₂O₃, TiO, TiC, and Ti with the increasing temperature^[13]. The reaction of TiO to TiC has the lowest Gibbs free energy in the six reactions above, which indicates that TiC can be generated at a higher reaction temperature. Theoretical calculation shows that the reaction temperature of TiO to TiC is 1 271 °C at normal atmospheric pressure, and the heat required for the reaction is above 500 kJ/mol. So when the TiC powders are synthesized by det-

onation shock, the reaction mechanism is different because of the characteristics of high temperature, high pressure and short reaction time. In this paper, the detonation parameters of HMX possess the pressure of 30 GPa, the temperature of 3 800 K, the heat of 1 697 kJ/mol, and the action time of detonation shock wave is only a few microseconds. Combining with analysis of the XRD patterns, the synthesis process of TiC powder under detonation shock wave was discussed preliminarily. When the shock wave acts on the precursors, the products of titanium dioxide by carbothermic method does not undergo the process of Ti_4O_7 , Ti_3O_5 , Ti_2O_3 , but directly to TiC and CO. This is the reason why no other forms of titanium oxides are observed in Fig.2 except the residual titanium dioxide. Since the properties of titanium carbide and titanium dioxide are similar, the purification method is the focus of work in the future.

The solid state chemical reactions undergo diffusion, formation of new crystalline phases and grain growth. First, a product layer is formed on the surface of the reactant. The subsequent reaction depends on the diffusion of the reactant in the product layer and the rate of chemical reaction of the reactants. For solid state reactions, the diffusion rate is usually very slow. So in most cases, the diffusion of particles plays a controlling role. However, the time of detonation shock wave is very short and the diffusion degree of their mutual reaction can only reach 0.1 nm when the powder is synthesized at the diffusion rate of $10^{-8} \text{ cm}^2/\text{s}$ ^[17]. It is inferred that nano-TiC powders can hardly be obtained in this processing, which was not consistent to the results confirming the existence of nano-TiC. So it is clear that the reaction by shock wave follows the solid state reaction, but it is quite different from the solid state reaction under normal conditions, for it has the characteristics of faster diffusion process and shorter reaction time. According to the detonation shock wave theory, a large number of dislocations produced by shock wave in materials will cause the decrease of diffusion activation energy. In addition, the plastic flow and deformation of materials will lead to the formation of slip bands and vortices at the interface, so that the atoms diffuse following the dislocations, twinning, and slip bands, which makes diffusion coefficients of solid materials increase significantly under the action of shock waves.

It was showed that the powder synthesized produce a lot of defects and lattice distortion by detonation shock waves^[18]. Theoretically, the density of lattice distortion can reach 10^{12} to 10^{13} cm^{-2} by the detonation shock waves. These defects can reduce the Gibbs free energy of nucleation and accelerate the formation and growth of the nucleation. Moreover, CO gas is released, and the heat transfer rate of gas is higher than that of solid material, which improves the mixing of reactants and promotes the powder synthesized to a certain extent.

3 Conclusion

The nano-TiC and TiC_x ($x < 1$) with the particle size of less than 50 nm were synthesized by detonation shock method. It is believed that although the mechanism of synthesizing nano-TiC by detonation shock wave follows the solid state reaction, it is quite different from the traditional solid state reaction because of the high temperature, high pressure and short action time of detonation shock wave. Compared to the traditional carbothermic method, the reaction by detonation shock wave of nano-TiC does not go through the order of Ti_4O_7 , Ti_3O_5 , Ti_2O_3 , but directly to TiC and CO. The effect of detonation shock wave leads to dislocation, slip band, vortex, defect and lattice distortion in the precursors, and CO gas was produced in the reaction process. These promotes the synthesis of nanometer TiC to a certain extent.

References:

- [1] LIU Y, ZENG L K. Titanium carbide ceramics and their applications [M]. Beijing: Chemical Industry Press, 2008.
- [2] CHEN Y Y, ZOU Z G, LONG F. Synthesis of TiC-based cermet and the status-quo of its research and application [J]. *Titanium Industry Progress*, 2007, 24(3): 5–9. DOI: 10.3969/j.issn.1009-9964.2007.03.002.

- [3] GRITZALIS D. Reliability, quality and safety of software-intensive systems [M]. Boston: Springer, 1997. DOI:10.1007/978-0-387-35097-4.
- [4] OUCHI H, NAGANO K, HAYAKAWA S. Piezoelectric properties of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ — PbTiO_3 — PbZrO_3 solid solution ceramics [J]. *Journal of the American Ceramic Society*, 1965, 48(12): 630–635. DOI: 10.1111/j.1151-2916.1965.tb14694.x.
- [5] MORELLI T, FOLEY J, LIEBERMAN L, et al. Pet-N-punch: upper body tactile/audio exergame to engage children with visual impairments into physical activity [C]// Proceedings of Graphics Interface 2011. St. John's: ACM, 2011: 223–230.
- [6] 王金淑, 周美玲, 张久兴, 等. 自蔓延法制备 TiC 粉末的研究 [J]. 北京工业大学学报, 1998, 24(3): 29–33.
WANG J S, ZHOU M L, ZHANG J X, et al. A study on titanium carbide produced by combustion synthesis [J]. *Journal of Beijing Polytechnic University*, 1998, 24(3): 29–33.
- [7] LOHSE B H, CALKA A, WEXLER D. Effect of starting composition on the synthesis of nanocrystalline TiC during milling of titanium and carbon [J]. *Journal of Alloys and Compounds*, 2005, 394(1/2): 148–151. DOI: 10.1016/j.jallcom.2004.09.074.
- [8] PREISS H, BERGER L M, SCHULTZE D. Studies on the carbothermal preparation of titanium carbide from different gel precursors [J]. *Journal of the European Ceramic Society*, 1999, 19(2): 195–206. DOI: 10.1016/S0955-2219(98)00190-3.
- [9] KOC R, FOLMER J S. Carbothermal synthesis of titanium carbide using ultrafine titania powders [J]. *Journal of Materials Science*, 1997, 32(12): 3101–3111. DOI: 10.1023/A:1018634214088.
- [10] 郭海明, 舒武炳, 乔生儒, 等. 化学气相沉积碳化钛的热力学和动力学研究 [J]. 材料工程, 1998(10): 25–29.
GUO H M, SHU W B, QIAO S R, et al. Thermodynamic and kinetic studies on chemical vapor deposition process of TiC [J]. *Journal of Materials Engineering*, 1998(10): 25–29.
- [11] 陈灿坤, 柳忠元, 向建勇, 等. 机械合金化制备碳化钛纳米粉体的合成机理研究 [J]. 燕山大学学报, 2012, 36(2): 136–140. DOI: 10.3969/j.issn.1007-791X.2012.02.008.
CHEN C K, LIU Z Y, XIANG J Y, et al. Study on synthesis mechanism of nano-TiC powders prepared by mechanical alloying [J]. *Journal of Yanshan University*, 2012, 36(2): 136–140. DOI: 10.3969/j.issn.1007-791X.2012.02.008.
- [12] 王作山, 刘玉存, 郑敏, 等. 爆轰冲击波在有机隔板中衰减模型的研究 [J]. 应用基础与工程科学学报, 2001, 9(4): 316–319. DOI: 10.3969/j.issn.1005-0930.2001.04.004.
WANG Z S, LIU Y C, ZHENG M, et al. Study on the attenuating model of detonation shock wave in the PMMA gap [J]. *Journal of Basic Science and Engineering*, 2001, 9(4): 316–319. DOI: 10.3969/j.issn.1005-0930.2001.04.004.
- [13] SEN W. Preparation of micron titanium carbide powder by carbothermal reduction TiO_2 method [D]. Kunming: Kunming University of Science and Technology, 2011.
- [14] PREISS H, LUTZ-MICHAEL B, SCHULTZE D. ChemInform abstract: studies on the carbothermal preparation of titanium carbide from different gel precursors [J]. *ChemInform*, 1999, 30(17). DOI: 10.1002/chin.199917295.
- [15] 文明芬, 王秋萍, 陈靖, 等. 纳米二氧化钛晶型互变的研究 [J]. 功能材料, 2004, 35(5): 651–653. DOI: 10.3321/j.issn:1001-9731.2004.05.042.
WEN M F, WANG Q P, CHEN J, et al. Study on the crystal transformation of nano-titania [J]. *Journal of Functional Materials*, 2004, 35(5): 651–653. DOI: 10.3321/j.issn:1001-9731.2004.05.042.
- [16] 杨筠, 林志明, 崔猛, 等. Si 粉在空气中燃烧合成 Si_3N_4 粉体 [J]. 无机材料学报, 2007, 22(4): 590–594. DOI: 10.3321/j.issn:1000-324x.2007.04.003.
YANG J, LIN Z M, CUI M, et al. Synthesis of Si_3N_4 by silicon combustion in air [J]. *Journal of Inorganic Materials*, 2007, 22(4): 590–594. DOI: 10.3321/j.issn:1000-324x.2007.04.003.
- [17] 王军霞, 杨世源, 贺红亮, 等. PZT95/5 粉体的冲击合成反应机理初探 [J]. 高压物理学报, 2007, 21(3): 322–326. DOI: 10.11858/gywlxb.2007.03.018.
WANG J X, YANG S Y, HE H L, et al. Study on the mechanism of PZT95/5 powder synthesis by shock waves [J]. *Chinese Journal of High Pressure Physics*, 2007, 21(3): 322–326. DOI: 10.11858/gywlxb.2007.03.018.
- [18] 王军霞, 杨世源, 贺红亮, 等. 冲击波合成 $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ 粉体的结构和特性 [J]. 硅酸盐学报, 2005, 33(6): 718–722. DOI: 10.3321/j.issn:0454-5648.2005.06.012.
WANG J X, YANG S Y, HE H L, et al. Structure and properties of $\text{Pb}(\text{Zr}_{0.95}\text{Ti}_{0.05})\text{O}_3$ powder synthesized by shock-wave technique [J]. *Journal of the Chinese Ceramic Society*, 2005, 33(6): 718–722. DOI: 10.3321/j.issn:0454-5648.2005.06.012.

(责任编辑 王小飞)