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先驱体转化法制备高性能碳化硼陶瓷材料研究进展

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摘 要: 碳化硼(B_4C)是一种性能优良的特种陶瓷, 在军事、核工业、航空航天等领域有着广泛的应用。近年来,采用先驱体转化法制备碳化硼陶瓷得到了长足的发展。相比碳化硼材料的其它制备方法, 先驱体转化法具有元素组成简单、成型性好、陶瓷产率高、能耗低等优势, 在制备碳化硼粉体、纤维、介孔材料、微球等方面有着广泛的应用。本文综述了先驱体转化法制备碳化硼陶瓷的最新研究进展, 着重介绍了碳化硼先驱体的合成及应用, 并对先驱体转化法制备碳化硼陶瓷的发展方向和应用前景进行了展望。

关 键 词: 碳化硼; 先驱体; 聚碳硼烷; 先驱体转化法; 综述

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Progress of Advanced Boron Carbide Ceramic Materials Prepared by Precursor Derived Method

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Abstract: Boron carbide (B_4C) is a kind of advanced ceramics with excellent properties, which has been widely applied in military, nuclear, aerospace, and other high-tech fields. The fabrication of boron carbide by precursor derived method has been well developed in recent years. Comparing with other preparative approaches, the precursor derived method has a variety of advantages including simple elemental composition, good formability, high ceramic yield, and low energy consumption, which has been widely applied to prepare boron carbide powder, fibers, mesoporous ceramics and ceramic microspheres. In this paper, current development of boron carbide prepared by precursor derived method was reviewed. Synthesis and application of boron carbide precursors were mainly discussed. In addition, the future efforts and application prospects of precursor-derived boron carbide ceramics were also analyzed.

Key words: boron carbide; precursor; polycarborane; precursor derived method; review

碳化硼陶瓷具有高熔点(2450℃)、高硬度(29.1 GPa)、大中子捕获面(600 barns)、低密度(2.52 g/cm)、较好的化学惰性、优良的热学和电学性能等, 是除了金刚石、立方氮化硼之外最坚硬的物质[1-2]。基于上述特性, 碳化硼除了大量被用作磨料之外, 还可以用于制备各种耐磨零件、热电偶元件、高温半导体、宇宙飞船上的热电转化装置、防弹装甲、反应堆控制棒与屏蔽材料等[3-4]。碳化硼早在 1858 年就被发现, 而化学计量比的化合物(B_4C)直到 1934 年才被制备出来。经过了几十年的发展, 研究人员发明了多种制备碳化硼陶瓷的方法, 主要包括: 碳热还原法、镁热还原法、元素直接合成法、溶剂热

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法、化学气相沉积法和先驱体转化法等[5]。碳热还原法、镁热还原法、元素直接合成法和溶剂热法多用于制备碳化硼粉体，而化学气相沉积法和先驱体转化法多用于制备具有特殊形貌的碳化硼陶瓷[6]。

化学气相沉积法是借助气相化学反应，在基体表面上进行沉积而制备碳化硼[7-8]。该方法可用于制备薄膜和纤维等碳化硼材料，但在制备过程中存在沉积不均匀且制备规模较小等缺点，从而限制了该方法的发展。

先驱体转化法是采用有机聚合物为先驱体，经高温无机转化制备陶瓷材料的方法。自上世纪 70 年代, Yajima 等[9]开创这项技术以来，先驱体转化技术发展日趋完善，制备出多种陶瓷先驱体及相应陶瓷材料，其中最具有代表性的是以聚碳硅烷(Polycarbosilane, PCS)[10-11]、聚硅氮烷(Polysilazane, PSZ)[12]、聚硼氮烷(Polyborazine, PBZ)[13]和聚硅硼氮烷(polycarbosilazane, PBSZ)[12]制备的 SiC、SiCN、SiBCN 以及 BN 陶瓷。该方法具有成型方便、元素组成可设计、陶瓷化温度低和陶瓷产物性能可调控等优点。相比其他方法，由于有机先驱体具有溶解或熔融特性，该方法可通过成型和热处理获得传统工艺难以获得的先进碳化硼陶瓷材料[14]。

本文针对先驱体转化法制备碳化硼陶瓷，综述了碳化硼先驱体的合成和应用，并对其发展方向和应用前景进行展望。

1 碳化硼先驱体的合成

目前碳化硼先驱体根据其合成反应过程中是否引入氧元素可分为两类：含氧先驱体和无氧先驱体。含氧碳化硼先驱体一般由溶胶–凝胶法通过硼酸与多羟基碳源反应得到，而无氧碳化硼先驱体主要由无氧硼源与碳源通过化学反应进行制备。

1.1 含氧碳化硼先驱体的合成

近年来，研究发现将硼酸与多羟基化合物反应制备碳化硼陶瓷，可使先驱体中硼源和碳源分散得更加均匀，可在较低温度下获得粒度更加均匀的碳化硼陶瓷粉末。2002 年，Sinha 等[25]用硼酸水溶液与柠檬酸反应形成凝胶，干凝胶在 700℃下裂解后，再在 1450℃下烧结得到碳化硼粉体(陶瓷产率 25%，硼含量 68.8%)。随后，研究人员又采用硼酸与丙三醇、酒石酸、甘露醇、蔗糖、葡萄糖等多羟基碳源反应制备碳化硼[15-17,20-22,26]，优化了反应条件，得到了粒度更均匀、自由碳含量更低的碳化硼粉体。Barros[23]和 Ikuo[24]等以聚乙烯醇和硼酸为原料，将硼酸溶液缓慢滴加到聚乙烯醇溶液中生成含氧的碳化硼先驱体聚乙烯醇硼酸酯(PVBO)。该先驱体在 120℃完全干燥后，再在 450~700℃和 1300℃下分别处理 2 h 和 5 h，即可得到碳化硼粉末。Chen 等[15]发现，将丙三醇引入改性 PVBO，可以提高凝胶反应效率，并改善颗粒的分散性。表 1 给出了关于含氧先驱体制备碳化硼陶瓷的总结。

1.2 无氧碳化硼先驱体的合成

目前采用的制备路线主要是通过硼氢化反应制备单体，单体再经过聚合得到先驱体[28]。早期，常采用高活性小分子硼源(硼烷或者卤化硼)制备碳化硼先驱体，但是此类先驱体陶瓷产率较低，且硼含量较低，无法满足应用需求[29-32]。Sneddon 等[33]合成了聚 2-乙烯基戊硼烷：首先由$[(\eta\text{-}C_5Me_5)IrCl_2]_2$催化乙烯与戊硼烷的反应，合成出 2-乙烯基戊硼烷单体；单体再经过加热聚合反应，合成出低聚烃基硼烷。该方法使先驱体中硼含量大幅提高，但由于该聚合物在较低温度(140℃)下会发生交联，限制了其作为先驱体的应用。

表 1 含氧先驱体制备碳化硼陶瓷

Table 1 Boron carbide ceramics prepared by oxygen-containing polymeric precursors

Serial no.	Polymeric precursors	Temperature/℃	Time/h	Ref.
1	Mixed solution of PVA, H_3BO_3 and glycerine	1200–1500	3	[15]
2	Reaction product of glycerin, tartaric acid and H_3BO_3	1250	0–5	[16]
3	Reaction product of d-mannitol, H_3BO_3	1500	3	[17]
4	Reaction product of tetramethyl/burate and resol,	1270	1−3	[18-19]
5	Condensed product of H_3BO_3 and mannitol product	1250	5	[20]
6	Reaction product of H_3BO_3 and sucrose	1300-1600	2−3	[21]
7	Condensation product of H_3BO_3 and glycerin	1250	5	[22]
8	Condensation product of PVA and H_3BO_3	1000	−	[23-24]
9	Mixed solution of citric acid and H_3BO_3	1450	2	[25]
10	Solution product of H_3BO_3 and glucose	1400	−	[26]
11	Condensation product of H_3BO_3 and 2-hydroxy benzyl alcohol	1500	4	[27]

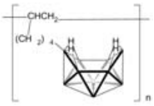
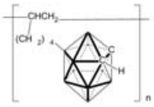
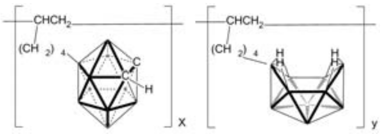
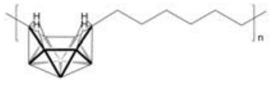
针对碳化硼(B_4C)的结构特征[1], 研究人员将十硼烷、碳硼烷等引入先驱体, 旨在提高先驱体中硼含量, 使其更接近化学计量比[34-35]。Seyferth 等[36-37]用二元胺、二元膦和二氰化物与十硼烷反应合成了一系列基于十硼烷的聚合物, 为制备碳化硼先驱体奠定了基础。

Pender 等[38-39]在 $Cp_2Ti(CO)_2$ 催化下利用 1,5-己二烯和十硼烷反应合成了 6-己烯十硼烷单体, 然后采用 $Cp_2ZrMe_2/B(C_6F_5)_3$ 催化体系完成了该单体的配位聚合反应, 合成出十硼烷在聚合物支链上的聚 6-己烯基十硼烷先驱体, 该先驱体分子量达到 4000 g/mol, 陶瓷产率达到 65%(1000℃)。Forsthoefel 等[40]使用相同的 Zr 催化剂, 用邻碳硼烷代替十硼烷制备了聚 6-己烯基邻碳硼烷先驱体, 但该先驱体分子量仍然较小, 只有 4000 g/mol。此外, 由于该邻碳硼烷的稳定性好, 难以实现低温交联, 陶瓷化过程中容易整体挥发脱除, 从而导致该先驱体的陶瓷产率极低(<20%)。为了避免上述问题, Forsthoefel 引入 6-己烯十硼烷进行共聚, 从而使先驱体的分子量提高到 8000 g/mol, 而且由于 6-己烯十硼烷产生了交联作用, 从而大幅提高了该先驱体的陶瓷产率(75.0%)。

先驱体的可纺性是衡量先驱体加工性能的重要指标之一, 一般可以用纺丝时的连续无断头时间和连续无断头长度来评价先驱体的可纺性[41]。为了得到可纺丝的碳化硼先驱体, 文献[42-43]制备了 6-降冰片烯基十硼烷以及 6-环辛烯基十硼烷单体, 并且利用 Grubbs Ⅰ、Ⅱ 代催化剂使其进行烯烃开环复分解聚合, 得到十硼烷侧链结构的新型硼碳陶瓷先驱体—聚 6-环辛烯基十硼烷和聚 6-降冰片烯基十硼烷, 其分子量可达 20000~40000g/mol。该技术的突破为先驱体转化法制备碳化硼纤维等特殊形貌材料的研究奠定了重要基础。Zhang 等[44]在制备先驱体时引入 1,5-己二烯, 在 Grubbs II 催化下进行共聚合反应, 从而在先驱体链中引入了柔性链, 改善了先驱体的溶解性。

表 2　不同先驱体的组成、合成条件及陶瓷产率

Table 2　Composition, synthetic condition, and ceramic yield of different precursors

Serial no.	Polymeric precursors	Catalyst	Ceramic yield/%	Ref.
1		$Cp_2ZrMe_2/B(C_6F_5)_3$ or $(Ind)_2ZrMe_2/B(C_6F_5)_3$	65.0	[38,39]
2		$Cp_2ZrMe_2/B(C_6F_5)_3$	<20.0	[40]
3		$Cp_2ZrMe_2/B(C_6F_5)_3$	75.0	[40]
4		Grubbs Ⅰ or Ⅱ	64.5	[42-43]
5		Grubbs Ⅰ or Ⅱ	60.0	[42-43]
6		$PtBr_2$	73.0	[46]
7		$PtBr_2$	82.0	[46]
8		Grubbs Ⅱ	72.5	[44]

十硼烷分子具有巢式结构，其6,9位的氢相对较活泼[45], Yu等[46]结合这一特点，采用Sneddon等[47-48]报导的(Bmim)BF_4离子液催化体系，合成了6-降冰片烯基十硼烷和6-己烯基十硼烷单体，在$PtBr_2$催化下进行了十硼烷和二烯烃的连续硼氢化聚合，合成出聚6-降冰片烯基十硼烷和聚6-己烯基十硼烷。其中十硼烷首次被引入到先驱体的主链结构中，为高性能聚烯基十硼烷的设计合成提供了新思路。表2给出了关于无氧先驱体制备碳化硼陶瓷的总结。

2 不同形貌的碳化硼陶瓷材料的制备

2.1 碳化硼粉体的制备

当前，含氧碳化硼陶瓷先驱体的主要应用是制备碳化硼粉体。采用含氧碳化硼先驱体制备碳化硼陶瓷，可使碳源和硼源在分子水平上均匀混合(图1(a))，不仅降低了反应温度，减少了硼源的损失，而且可得到粒度更加均匀的陶瓷粉末(图1(b))[49]。但含氧先驱体在本质上还是利用碳还原氧化硼得到碳化硼陶瓷，反应温度依然较高，且残留的游离碳会影响陶瓷的性能[50-51]。

2.2 碳化硼纤维的制备

无氧碳化硼陶瓷先驱体主要含B、C与H三种元素，高温下H和一部分C会以小分子烷烃的形式脱除，陶瓷产物主要为碳化硼与自由碳。无氧先驱体具有陶瓷转变温度低和陶瓷产率高等优势，具有广阔的应用前景。2000年，Pender等[39]采用$6,6'\text{-}(CH_2)_6(B_{10}H_{13})_2$先驱体运用氧化铝模板法制备了$\phi$250 nm×25 μm的碳化硼纳米纤维(图2 (a))。2005年，Sneddon等[42]采用同样的方法以支链聚6-降冰片烯十硼烷为先驱体制备了ϕ250 nm×25 μm的碳化硼纳米空心圆柱体(图2(b))。在碳化硼陶瓷先驱体的分子量达到纺丝要求以前，碳化硼纳米纤维主要通过化学气相沉积[52]与模板法制备。在烯烃开环复分解聚合制备高分子量聚碳硼烷基础上，Danie等[53]采用聚6-降冰片烯十硼烷的四氢呋喃溶液进行了静电纺丝，通过高温烧结制备了直径在300~500nm的碳化硼纳米纤维(图2(c)和(d))。

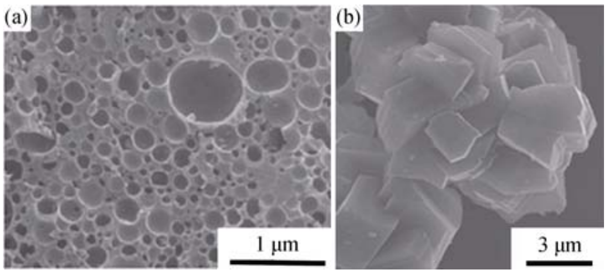


图1 聚乙烯醇硼酸酯600℃下热解产物的SEM照片(a)和1250℃下处理5 h所获得产物的形貌(b)[49]

Fig. 1 SEM image of the product of the PVBO precursor pyrolyzed at 600℃ (a); morphology of product obtained by heat treatment at 1250℃ for 5 h (b)[49]

2006年, Marta等[54]采用碳化硼先驱体与聚甲基碳硅烷(PMCS)、烯丙基氢化聚碳硅烷(AHPCS)共混制备了碳化硼/碳化硅复相陶瓷纤维(见图3)。与反应烧结[55]和热压烧结[56]等工艺制备复相陶瓷相比，该方法中碳化硼与碳化硅在分子水平进行混合，使得

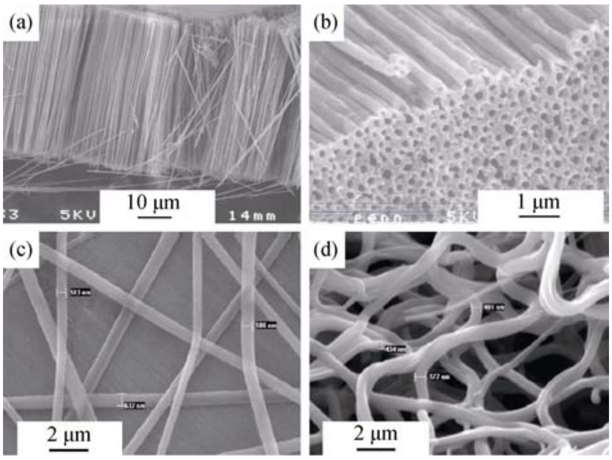


图2 碳化硼纳米线(a)[39]、碳化硼纳米空心圆柱体末端(b)[42]、静电纺丝得到的碳化硼纳米纤维(c, d)的SEM照片[53]

Fig. 2 SEM images of the boron carbide nanofibers (a)[39], the end of the boron carbide nanocylinders (b)[42], and the nanofibers obtained via electro-spinning (c, d)[53]

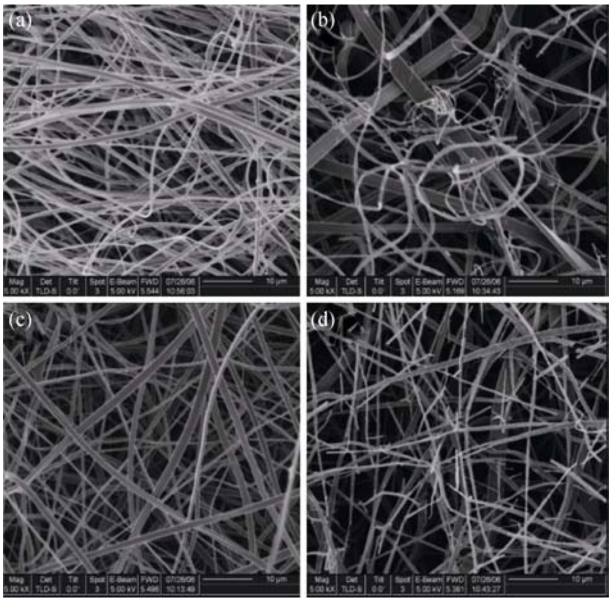


图3 聚合物纤维(a)以及分别在1000℃(b), 1300℃(c)和1600℃(d)裂解得到的碳化硼/碳化硅陶瓷纤维的SEM照片[54]

Fig. 3 SEM images of fiber (a) polymer fibers and the boron-carbide/silicon-carbide ceramic fibers obtained by pyrolysis at (b) 1000℃, (c) 1300℃ and (d) 1600℃[54]

两相混合更均匀, 且两相比例能够调节。

2.3　碳化硼介孔材料的制备

Borchardt 等[57]采用先驱体纳米浇注法, 以 6,6'-$(CH_2)_6(B_{10}H_{13})_2$ 先驱体浸渍二氧化硅模板, 制备了碳化硼有序介孔材料(图 4(a, b)), 800℃下烧结的产物其比表面积可达 778 m^2/g, 在大分子吸附、催化反应、药物存储等领域具有很好的应用前景[58]。Malenfant 等[59]以烯烃复分解反应合成的含有十硼烷的有机聚合物先驱体为基础, 采用嵌段共聚物在四氢呋喃溶液中进行自组装(图 4(c)), 1000℃氨气气氛下热解制备得到氮化硼有序介孔材料 (图 4(d))。

2.4　碳化硼陶瓷微球的制备

2016 年, 国防科学技术大学[60-61]在高分子量碳化硼先驱体合成的基础上, 利用先驱体良好的成形性, 经过成球、固化、不熔化、高温裂解等一系列步骤制备了碳化硼陶瓷空心微球(图 5)。空心微球的直径可达 1.0~1.5 mm, 壁厚 10~50 μm, 且球形度较高(97%), 可用于核聚变靶向材料[62]。Zhang 等[44]也利用碳化硼先驱体与二烯烃的共聚物制备了直径在 0.77 mm 左右的碳化硼多孔空心微球。

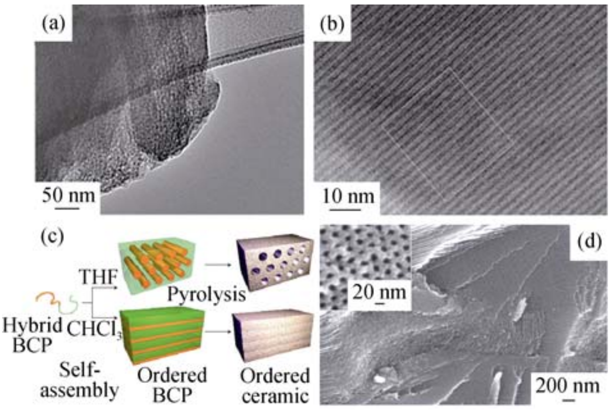


图 4　碳化硼有序介孔材料的 TEM 照片[57-58]

Fig. 4　TEM and SEM micrographs of ordered mesoporous boron carbide ceramics[57-58]

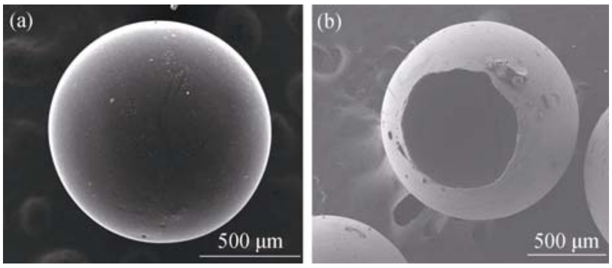


图 5　碳化硼空心微球的 SEM 照片[61]

Fig. 5　SEM micrographs of the prepared boron carbide microspheres[61]

3　结论

碳化硼是一种性能优良的特种陶瓷, 在军事、核工业、航空航天等领域有着广泛的应用前景。近年来, 采用先驱体转化法制备碳化硼陶瓷得到了长足的发展, 相比碳化硼材料的其它制备方法, 先驱体转化法具有元素组成简单、成型性好、陶瓷产率高、能耗低等优势, 在制备碳化硼粉体、纤维、介孔材料、微球等方面有着广阔的研究空间与应用前景。虽然先驱体转化法制备碳化硼陶瓷具有明显的优势, 但是还存在以下问题有待解决:

1) 含氧碳化硼先驱体虽然容易制备, 但是氧的存在会影响碳化硼陶瓷的致密性和高温性能。而无氧碳化硼先驱体的制备成本高, 主要由于十硼烷及碳硼烷等硼烷原料单体成本高, 同时, 单体及聚合过程中使用的催化剂价格昂贵。

2) 目前制备的先驱体硼含量偏低, 富余的碳在陶瓷化过程中无法彻底脱除, 因此, 合成近化学计量比的碳化硼先驱体, 进而制备近化学计量比的碳化硼陶瓷技术依然存在挑战。

3) 碳化硼陶瓷先驱体的种类较少, 特别是含有异质元素如铁、铝、锆、钛等的先驱体合成鲜有报道。

4) 目前先驱体转化法制备得到的碳化硼陶瓷, 其应用研究偏少。

针对上述问题, 应在以下方面进一步开展研究: (1)改进现有单体及先驱体的制备路线, 降低制备成本; (2)设计近化学计量比的先驱体, 或者在陶瓷化过程中脱除过多的碳, 从而制备出近化学计量比的碳化硼陶瓷; (3)进行先驱体设计, 以性能为导向, 合成含有异质元素的新型碳化硼陶瓷先驱体; (4)利用先驱体转化法可制备形状复杂的碳化硼陶瓷材料, 进一步加强所得碳化硼陶瓷的应用研究。

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