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液态聚硅氮烷的改性及在 SiCN 基复合陶瓷制备中的应用

Modification of Polysilazanes and their Application in the
Preparation of SiCN-based Ceramic Composites

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目 录

摘 要.....	I
Abstract.....	III
缩略语表	V
第一章 绪论	1
1.1 引言.....	1
1.2 聚硅氮烷先驱体的研究.....	3
1.2.1 氨解法	3
1.2.2 胺解法	6
1.2.3 肼解法	6
1.2.4 脱氢耦合	7
1.2.5 开环聚合	7
1.3 PBSZ 先驱体的研究.....	9
1.3.1 PBSZ 的聚合物合成路线	9
1.3.2 PBSZ 的单体合成路线	10
1.4 金属掺杂的聚硅氮烷先驱体的研究.....	12
1.4.1 含 Ti、Zr 聚硅氮烷先驱体的研究.....	12
1.4.2 含 Fe、Co、Ni 聚硅氮烷先驱体的研究	14
1.4.3 其他金属改性聚硅氮烷先驱体的研究.....	15
1.5 应用背景.....	16
1.5.1 陶瓷纤维	17
1.5.2 陶瓷基复合材料	17
1.5.3 其他应用	17
1.6 论文设想和目的.....	18
参考文献.....	19
第二章 实验部分	31
2.1 试剂和仪器.....	31
2.1.1 试剂	31
2.1.2 仪器设备	31
2.2 分析测试方法.....	32
2.2.1 FT-IR 测试方法	32
2.2.2 NMR 测试方法	32
2.2.3 GPC 测试方法	32
2.2.4 TGA 测试方法	33
2.2.5 XRD 测试方法	33
2.2.6 SEM 测试方法	33
2.2.7 TEM 测试方法	33
2.2.8 VSM 测试方法	33
2.3 实验步骤.....	34
2.3.1 合成实验	34
2.3.2 热交联实验	36
2.3.3 陶瓷化实验	36

参考文献.....	37
第三章 聚硅氮烷/二氯二茂钛杂化先驱体的交联与陶瓷化研究.....	39
3.1 引言.....	39
3.2 结果与讨论.....	40
3.2.1 CPSZ 先驱体的结构表征	40
3.2.2 杂化先驱体的交联.....	43
3.2.3 杂化先驱体的陶瓷化.....	46
3.2.4 陶瓷的结晶行为.....	48
3.2.5 陶瓷的微观形貌.....	50
3.2.6 陶瓷的热性能.....	52
3.3 本章小结.....	52
参考文献.....	53
第四章 含铁聚硅氮烷的合成及在磁性陶瓷制备中的应用.....	59
4.1 引言.....	59
4.2 结果与讨论.....	60
4.2.1 CPSZ 先驱体结构表征	60
4.2.2 PFSZ 先驱体的表征.....	60
4.2.3 先驱体的交联与陶瓷化.....	63
4.2.4 陶瓷的微观结构.....	66
4.2.5 陶瓷的性能.....	71
4.3 本章小结.....	73
参考文献.....	73
第五章 硼改性聚硅氮烷先驱体的交联与陶瓷化研究.....	79
5.1 引言.....	79
5.2 结果与讨论.....	80
5.2.1 原料表征.....	80
5.2.2 PBSZs 的交联.....	82
5.2.3 PBSZs 的陶瓷化.....	84
5.2.4 陶瓷的结晶行为.....	87
5.2.5 陶瓷的微观形貌.....	91
5.2.6 陶瓷的耐高温性能.....	93
5.3 本章小结.....	95
参考文献.....	96
第六章 总结与展望	101
6.1 总结.....	101
6.2 展望.....	102
附录：硕士期间发表成果	103
致 谢.....	105

Content

Abstract in Chinese	I
Abstract in English	III
Abbreviation	V
Chapter 1 Introduction	1
1.1 Introduction	1
1.2 Synthesis of polysilazanes	3
1.2.1 Ammonolysis	3
1.2.2 Aminolysis	5
1.2.3 Hydrazinolysis.....	6
1.2.4 Dehydrocondensation.....	6
1.2.5 Ring-opening reaction	7
1.3 Synthesis of polyboronsilazane	8
1.3.1 Polymer route	9
1.3.2 Monomer route.....	10
1.4 Metal modified polysilazane	12
1.4.1 Ti、Zr modified polysilazane	12
1.4.2 Fe、Co、Ni modified polysilazane.....	13
1.4.3 Other metal modified polysilazane	15
1.5 Applications	16
1.5.1 Ceramic fibres.....	16
1.5.2 Ceramic-matrix composites	17
1.5.3 Other applications	17
1.6 Scheme and objective of this dissertation	18
Reference	19
Chapter 2 Experimental	31
2.1 Materials and apparatus	31
2.1.1 Materials.....	31
2.1.2 Apparatus	31
2.2 Measurements	32
2.2.1 FT-IR.....	32
2.2.2 NMR.....	32
2.2.3 GPC.....	32
2.2.4 TGA.....	33
2.2.5 XRD	33
2.2.6 SEM.....	33
2.2.7 TEM	33
2.2.8 VSM	33
2.3 Experimental methods	34
2.3.1 Synthesis.....	34
2.3.2 Cross-linking	36
2.3.3 Ceramic conversion.....	36
Reference	37
Chapter 3 Preparation, cross-linking and ceramization of CPSZ/Cp₂TiCl₂ hybrid precursors	39

3.1 Introduction	39
3.2 Results and discussion	40
3.2.1 Characterization of CPSZ.....	40
3.2.2 Cross-linking of hybrid precursors.....	43
3.2.3 Ceramization of hybrid precursors	46
3.2.4 Crystallization of ceramics	48
3.2.5 Microstructure of ceramics.....	50
3.2.6 Thermostability of ceramics	51
3.3 Conclusions	52
Reference	53
Chapter 4 Preparation of SiCNFe magnetic ceramic derived from iron modified CPSZ	59
4.1 Introduction	59
4.2 Results and discussion	60
4.2.1 Characterization of CPSZ.....	60
4.2.2 Characterization of PFSZ	60
4.2.3 Cross-linking and ceramization of precursors.....	63
4.2.4 Microstructure of ceramics.....	66
4.2.5 Properties of ceramics	71
4.3 Conclusions	73
Reference	73
Chapter 5 Preparation, cross-linking and ceramization of boron modified CPSZ	79
5.1 Introduction	79
5.2 Results and discussion	80
5.2.1 Characterization of materials	80
5.2.2 Crosslinking of PBSZs	82
5.2.3 Ceramic conversion of PBSZs	84
5.2.4 Crystallization of ceramics	87
5.2.5 Microstructure of ceramics.....	91
5.2.6 Thermostability of ceramics	93
5.3 Conclusions	95
Reference	96
Chapter 6 Summary and forecast	101
6.1 Summary	101
6.2 Forecast	102
Appendix	103
Acknowledgements	105

摘要

聚合物先驱体陶瓷 (PDC) 法采用化学方法合成聚合物先驱体, 然后成型、热解制备陶瓷, 开辟了有机高分子制备无机陶瓷的新途径。PDC 法的优势在于可通过先驱体的分子设计从而控制陶瓷的组成和微结构, 从而调控陶瓷的性能。聚硅氮烷是一类重要的陶瓷先驱体, 其烧结制备 SiCN 和 Si₃N₄ 陶瓷具有良好的物理、化学和机械性能, 不仅是优良的耐高温材料, 在微电子器件、锂离子电池等方面也有着广阔的应用前景。

本文以促进聚合物先驱体交联, 提高陶瓷产率和陶瓷高温稳定性, 以及制备磁性功能陶瓷为目的, 设计和制备了一系列金属和硼掺杂改性的共聚聚硅氮烷, 对其进行交联和陶瓷化研究, 并评价最终陶瓷的耐高温性能和磁性能。采用傅立叶红外光谱 (FT-IR)、核磁共振 (NMR)、凝胶渗透色谱 (GPC) 等测试方法分析产物的化学结构、组成和分子量; 用 FT-IR、热重分析 (TGA)、X 射线衍射 (XRD)、扫描电镜 (SEM)、高分辨透射电镜 (TEM)、能谱仪 (EDS)、振动磁强计 (VSM) 等方法对先驱体的交联和陶瓷化产物的组成、热行为、结晶行为、微观结构和磁性能等进行表征。

首先, 采用 Cp₂TiCl₂ 与 CPSZ 共混制备了一系列不同 Ti 含量的含钛聚硅氮烷杂化先驱体 (PTSZ)。结果表明: Cp₂TiCl₂ 的引入促进了 PTSZ 先驱体中的脱氢耦合、硅氢加成反应, 有效地促进了先驱体的交联, 并最终提高了陶瓷产率, 在 1200 °C 时陶瓷产率可以达到 75.2%; 从先驱体到无机陶瓷的转换在 900 °C 基本完成, 得到无定型的陶瓷产物; 进一步升高温度, 陶瓷中开始出现结晶, Ti 元素主要以 TiC 的形式存在, 得到 SiCN/TiC 复相陶瓷。

其次, 以 Fe(acac)₃ 与 CPSZ 反应制备了一种液态的含铁聚硅氮烷先驱体 (PFSZ), 烧结后得到 SiCNFe 磁性陶瓷。结果表明, CPSZ 与 Fe(acac)₃ 之间发生了化学反应, Fe(acac)₃ 的加入使陶瓷产率提高约 25%; α-Fe 是陶瓷中唯一的磁性结晶, 大小为 10~20 nm, 均匀的分布在 SiCN(O)陶瓷基体中, 使得陶瓷具有良好的软磁性, 陶瓷中的 Fe 含量和磁性能都可以通过先驱体中的 Fe(acac)₃ 的引入量的改变来进行调控。

最后，利用二甲基胺硼烷（DMAB）与 CPSZ 的硼氢加成和脱氢耦合反应，制得了一系列不同硼含量的聚硼硅氮烷（PBSZ）先驱体。结果表明：DMAB 的引入使得先驱体中生成 B-N 键，并且促进了先驱体的交联；陶瓷产率得到明显提高；陶瓷中的硼以 BN 的形式存在，BN 抑制了陶瓷的结晶，抑制了 Si_3N_4 的分解，显著提高了陶瓷的耐高温性能，陶瓷致密度提高，表面孔洞和晶粒尺寸减小。

关键词：聚硅氮烷；改性；陶瓷复合材料；氮化硅；碳化硅

Abstract

The preparation of polymer derived ceramics (PDCs) involves synthesis of polymeric precursors, followed shaping, and final pyrolysis. The PDC route enabled significant technological breakthrough in ceramic science and technology, with polymers as starting materials. The composition and microstructure of ceramics are directly influenced by the molecular design of the preceramic precursors, thus there is an enormous potential in tuning the properties of the PDCs by using tailored polymers. Polysilazane (PSZ) is one of the important preceramic polymers. The PSZ-derived Si-C-N and Si₃N₄ ceramics show great physical, chemical and mechanical properties. They are not only used as high temperature resistant materials, but also promising in the fields of microelectronic devices and lithium ion battery, etc.

In order to improve the cross-linking of the polymeric precursors, increase the ceramic yield, improve the thermal stability of the final ceramics and prepare the magnetoceramics, our research interests focus on the metal and boron-modified copolysilazanes (CPSZs), including their cross-linking and ceramization. Moreover, the thermal stability and magnetic properties of the final ceramics were evaluated. The structure, composition and molecular weight of the precursors were investigated by Fourier transformed infrared (FT-IR) spectroscopy, nuclear magnetic resonance (NMR), and gel permeation chromatography (GPC). The composition, crystallization, microstructure and magnetic properties of resultant ceramics were studied by FT-IR, thermal gravimetric analysis (TGA), X-ray diffraction (XRD), scanning electron microscope (SEM), high resolution transmission electron microscopy (HRTEM) and vibrating sample magnetometer system (VSMs).

Firstly, CPSZ/Cp₂TiCl₂ hybrid precursors (PTSZ) with different Ti content were prepared by the blending of CPSZ and Cp₂TiCl₂. It was suggested that the introduction of Cp₂TiCl₂ improved the cross-linking of the hybrid precursors via transamina, hydrosilation and dehydrocoupling reactions, which was responsible for a relatively high ceramic yield of 75.2% at 1200 °C. The polymer-to-ceramic conversion

was complete at 900 °C, and it gave an amorphous ceramic. Further heating induced partial crystallization, and the Ti element was in the form of TiC in the SiCN/TiC composite ceramics.

Secondly, SiCNFe magnetoceramics were obtained by the pyrolysis of iron-modified CPSZ (PFSZ) precursors which were synthesized by using CPSZ and Fe(acac)₃ as starting materials. The results showed the chemical reaction between the CPSZ with Fe(acac)₃ did occur. The ceramic yield of PFSZ precursor is ca. 25% higher than original PSZ. It was also suggested that α-Fe nanoparticles (10~20 nm) were uniformly dispersed in amorphous SiCN(O) matrix, which might be responsible for the soft magnetization of the resultant SiCNFe ceramics. Moreover, iron contents and magnetic properties of SiCNFe ceramics could be easily controlled by the amount of Fe(acac)₃ in the precursors.

Finally, boron-modified polysilazane (PBSZ) precursors were prepared by the chemical reactions of CPSZ and dimethylamine borane (DMAB), involving hydroboration and dehydrocoupling reactions. The results indicated that the B-N covalent bonds were formed in the PBSZ precursors. The introduction of DMAB improved the cross-linking of precursors and the ceramic yields. It was suggested that the BN suppressed the crystallization of ceramics and the decomposition of Si₃N₄. As a result, the size of micropores and crystallite dimension were reduced, while the thermal stability and the density of ceramics were dramatically promoted.

Keywords: Polysilazane; Modification; Ceramic composite; Silicon nitride; Silicon carbide

缩略语表

BN.....	氮化硼 (Boron nitride)
CFRCMC	连续纤维增强陶瓷基复合材料 (Continuous-fiber-reinforced ceramic matrix composite)
CMC.....	陶瓷基复合材料 (Ceramic matrix composite)
CPSZ.....	共聚聚硅氮烷 (Co-polysilazane)
CVD.....	化学气相沉积法 (Chemical vapor deposition)
DMAB.....	二甲基胺硼烷 (Dimethylamine borane)
EDS.....	X 射线能谱 (Energy dispersive spectroscopy)
FT-IR.....	傅立叶红外光谱法 (Fourier transformed infrared)
GPC.....	凝胶渗透色谱 (Gel permeation chromatography)
NMR.....	核磁共振谱 (Nuclear magnetic resonance)
PBSZ.....	聚硼硅氮烷 (Polyborosilazane)
PCS.....	聚碳硅烷 (Polycarbosilane)
PS.....	聚硅烷 (Polysilane)
PSZ.....	聚硅氮烷 (Polysilazane)
SEM.....	扫描电镜 (Scanning electron microscope)
Si-B-C-N.....	硅硼碳氮 (Silicon boron carbon nitride)
SiC.....	碳化硅 (Silicon carbide)
SiCN.....	硅碳氮 (Silicon carbon nitride)
Si ₃ N ₄	氮化硅 (Silicon nitride)
TADB.....	Cl ₃ Si-NH-BCl ₂ (Trichlorosilylaminodichloroborane)
TEM.....	透射电镜 (Transmission electron microscopy)
TGA.....	热重分析 (Thermal gravimetric analysis)
THF.....	四氢呋喃 (Tetrahydrofuran)
VSM.....	振动样品磁强计 (Vibrating sample magnetometer)
XRD.....	X 射线粉末衍射 (X-ray diffraction)

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