



LES CERAMIQUES DERIVEES DE PRECURSEURS

- 1. Polymer Derived Ceramics
- 2. Atomic Layer Deposition

Philippe MIELE



Institut Européen des Membranes - IEM (UMR ENSCM/UM/CNRS 5635) Montpellier, France







Precursors Derived Ceramics - Contexte international

Mot clé : ceramic, période 1995 – 2015 → 175.500 résultats

CHINA	21 %
USA	16 %
JAPAN	11 %
GERMANY	7,5 %
INDIA	5 %
FRANCE	4,7 %
SOUTH KOREA	4,7 %
ENGLAND	4,5 %
RUSSIA	3,5 %
SPAIN	3,3 %

Mots clés : ceramic + precursor, période 1995 – 2015 → 11.000 résultats

CHINA	21 %
USA	15 %
GERMANY	10 %
JAPAN	9,2 %
INDIA	7,6 %
FRANCE	6,5 %
SOUTH KOREA	4,5 %
BRAZIL	4,4 %
SPAIN	4,3 %
ENGLAND	3,9 %

1^{er} français : 13^{ème} auteur 2^{ème} français : 21^{ème} auteur

Precursors Derived Ceramics - Contexte international

Mots clés : ceramic + precursor, période 1995 – 2015 ➔ 11.000 résultats

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Citations \rightarrow h = 118

Precursors Derived Ceramics - Contexte international

Mot clé : ceramic + precursor, période 1995 – 2015 + Europe → 3.800 résultats

GERMANY	27,1 %
FRANCE	18,2 %
SPAIN	12,0 %
ENGLAND	11,04 %
ITALY	9,3 %
POLAND	4,2 %
ROMANIA	3,8 %
PORTUGAL	2,9 %
SWITZERLAND	2,7 %

GERMANY	1000
FRANCE	600
SPAIN	440
ENGLAND	400
ITALY	340
POLAND	160
ROMANIA	148

Precursors Derived Ceramics - Contexte national

Mot clé : ceramic + precursor, période – 2015 + France → ~ 700 résultats



nombre



Precursors Derived Ceramics - Contexte national

Mot clé : ceramic + precursor, période − 2015 + France → ~700 résultats



Precursors Derived Ceramics – Historique/International

- Bildung siliciumorganischer Verbindungen. V. Die Thermische Zersetzung von Si(CH₃)₄ und Si(C₂H₅)₄. G. Fritz and B. Raabe, Z. Anorg. Allg. Chem., 286, 149–67. 1956.
- The Preparation of **Phosphorus-Nitrogen** Compounds as Non-Porous Solids. F. W. Ainger and J. M. Herbert, pp. 168–82 in *Special Ceramics*, Edited by P. Popper. Academic press, New York, **1960**.
- Inorganic Polymers and Ceramics. G. Chantrell and P. Popper; pp. 87–103 in Special Ceramics, Edited by P. Popper. Academic Press, New York, 1965.
- Continuous Silicon Carbide Fiber of High Tensile Strength". S. Yajima, J. Hayashi and M. Imori, *Chem. Lett.*, 4 [9] 931–4 (1975).
- Development of High Tensile Strength Silicon Carbide Fibre Using an Organosilicon Polymer Precursor". S. Yajima, Y. Hasegawa, K. Okamura and I. Matsuzawa, Nature (London), 273, 525–7 (1978).
- High-purity Polycrystalline Ceramics From Organometallic Precursors. K. S. Mazdiyasni. American Ceramic Society Bulletin Volume: 60 Issue: 3 (1981) p. 350-350. ISSN: 0002-7812.
- Polymethylchlorosilane and its Derivatives as Precursors to Silicon-Carbide Ceramic Fibers and Shapes. R. H. Baney, J. H. Gaul, T. K. Hilty. *American Ceramic Society Bulletin*. Volume: 60 Issue:
 3 Pages: 374-374 Published: 1981

1950-1981 : 7 références dont ~4 dans le domaine des fibres SiC à hautes performances thermomécaniques

Precursors Derived Ceramics – Historique/National

Physica B 158 (1989) 229–230 North-Holland, Amsterdam

STUDY OF THE POLYMER TO CERAMIC EVOLUTION INDUCED BY PYROLYSIS OF ORGANIC PRECURSOR.

C.LAFFON*, A.M.FLANK*, P.LAGARDE*, E.BOUILLON°

*LURE, Bâtiment 209D, U.P.S., 91405-ORSAY (France) ^oLaboratoire de Chimie du Solide, Université de Bordeaux I, 33405-TALENCE (France)

Abstract: The structure of a precursor: the polycarbosilane, has been followed during pyrolysis up to 1600° C. A continuous evolution is observed, leading to a nucleation of SiC clusters followed at higher temperature by a growth of the SiC crystalline phase. The structure keeps the memory of the precursor up to 1400° C.

A New Way to SiC Ceramic Precursors by Catalytic Preparation of Preceramic Polymers **

By Bruno Boury, Leslie Carpenter, and Robert J. P. Corriu*

The preparation of ceramic materials by organometallic processes has opened a new chapter in chemical research. In

 [*] Prof. R. J. P. Corriu, B. Boury, L. Carpenter Unité Mixte CNRS/RP/USTL
 Université de Montpellier II – case 007 Place Eugène Bataillon, F-34095 Montpellier Cédex 5 (France)

[**] This work was supported by CNRS and Rhône-Poulenc Company.

Angew. Chem. Int. Ed. Engl. 29 (1990) No. 7

© VCH Verlagsgesellschaf.

Composites Science and Technology 37 (1990) 7-19

Pyrolysis of Polysilazanes: Relationship between Precursor Architecture and Ceramic Microstructure

F. Sirieix, P. Goursat

Laboratoire de Céramiques Nouvelles, Université de Limoges, UA CNRS no. 320, 123 Avenue A. Thomas, 87060 Limoges, France

A. Lecomte & A. Dauger

Ecole Nationale Supérieure de Céramiques Industrielles. UA CNRS no. 320, 47 Avenue A. Thomas, 87065 Limoges, France

(Received 19 July 1988; revised version received 15 November 1988; accepted 14 June 1989)

ABSTRACT

The pyrolysis of polysilazanes to silicon carbo-nitride has been studied on account of their potential as precursors for ceramic matrices. First, a

New Poly(carbosilane) Models. 4. Derivatization of Linear Poly[(methylchlorosilylene)methylene]: Application to the Synthesis of Functional Poly(carbosilanes) Possessing a Poly[(methylsilylene)methylene] Backbone

E. Bacqué, J.-P. Pillot,* M. Birot, J. Dunoguès,* and P. Lapouyade

Laboratoire de Chimie Organique et Organométallique (URA 35, CNRS), <mark>Université Bordeaux</mark> I, 351, Cours de la Libération, F-33405 Talence Cédex, France

E. Bouillon and R. Pailler

Laboratoire des Composites Thermostructuraux, UM 47, CNRS-SEP-UB1, Europarc 3, Avenue Léonard de Vinci, F-33610 Pessac, France

Received February 21, 1990. Revised Manuscript Received December 20, 1990

Precursors Derived Ceramics – Historique/National

Chem. Mater. 1993, 5, 260-279

Reviews

Preceramic Polymer Routes to Silicon Carbide

Richard M. Laine*

Departments of Materials Science and Engineering, and Chemistry, University of Michigan, Ann Arbor, Michigan 48109-2136

Florence Babonneau

Laboratoire Chimie de la Matiere Condensée, Université de Pierre et Marie Curie, Paris, France

Received October 12, 1992. Revised Manuscript Received December 21, 1992

Chem. Mater. 1995, 7, 299-303

Boron Nitride Matrices and Coatings Obtained from Tris(methylamino)borane. Application to the Protection of Graphite against Oxidation

B. Bonnetot,* F. Guilhon, J. C. Viala, and H. Mongeot

Laboratoire de Physico-chimie Minérale Ib, CNRS 116, U.C.B. LYON I, 43. Bd du 11 Novembre 1918, 69622 Villeurbanne Cedex, France

Received July 18, 1994. Revised Manuscript Received November 21, 1994[®]

Chem. Mater. 2001, 13, 1700-1707

Chemically Derived BN Ceramics: Extensive ¹¹B and ¹⁵N Solid-State NMR Study of a Preceramic Polyborazilene

Christel Gervais,[†] Jocelyne Maquet,[†] Florence Babonneau,^{*,†} Christophe Duriez,[‡] Eric Framery,[‡] Michel Vaultier,[‡] Pierre Florian,[§] and Dominique Massiot[§]

Chimie de la Matière Condensée, Université Pierre et Marie Curie/CNRS, Paris, France, Synthèses et électrosynthèses organiques, Université Rennes I, Rennes, France, and CRMHT, CNRS. Orléans. France

Received December 11, 2000. Revised Manuscript Received February 8, 2001



Chem. Rev. 1995, 95, 1443-1477

Marc Birot, Jean-Paul Pillot, and Jacques Dunoguès*

Laboratoire de Chimie Organique et Organométallique, U.R.A. CNRS 35, Université Bordeaux I, 351 cours de la Libération, F-33405 Talence Cédex, France

Received November 10, 1994 (Revised Manuscript Received May 11, 1995)

I. General Introduction

I. General Introduction A. Scope and Limitations

Contents

1443 1444

Among the high-performance non-oxide ceramics, silicon carbide (SiC) and nitride (Si₃N₄) offer unique

J. Mater. Chem., 1999, 9, 757-761	JOURNAL OF
Conversion of $B(NHCH_3)_3$ into boron nitride and polyborazine fibres and tubular BN structures derived therefrom	Mater
David Cornu,*" Philippe Miele," René Faure, ^b Bernard Bonnetot," Henri Mongeot" and <mark>Jean Bouix</mark> "	ials
^{(L} aboratoire des Multimatériaux et Interfaces, UMR CNRS 5615, Université Claude Bernard— Lyon I, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France. E-mail: cornu@univ-lyon1.fr	CHEMISTRY
^b Laboratoire de Chimie Analytique 2, LICAS, Université Claude Bernard—Lyon 1, 43 bd du 11 novembre 1918, 69622 Villeurbanne Cedex, France	

Received 22nd October 1998, Accepted 10th December 1998



FULL PAPER

Adv. Funct. Mater. 2002, 12, No. 3, March

Boron Nitride Fibers Prepared from Symmetric and Asymmetric Alkylaminoborazines

By Bérangère Toury, Philippe Miele,* David Cornu, Henri Vincent, and Jean Bouix

Polymer-Derived Ceramics (PDCs): *Methodology*



Polymer-Derived Ceramics (PDCs): *Methodology*



Non Oxide (Carbo)Nitride PDCs



H. Holleck, V. Schier, Surf. Coat. Technol., 1995, 76-77, 328

- Thermally and chemically stable materials,
- → Wide band gap materials
 - Insulators, or semi-conductors

Other specific properties (tenacity, hardness, photocatalytic, ...)

Non Oxide (Carbo)Nitride PDCs



H. Holleck, V. Schier, Surf. Coat. Technol., 1995, 76-77, 328

- Thermally and chemically stable materials,
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Other specific properties (tenacity, hardness, photocatalytic, ...)

Non Oxide (Carbo)Nitride PDCs : Selected applications



Molecular precursors of boron nitride

- Borazine based precursors (B₃N₃ core : basical pattern of *h*-BN)
- High ceramic yield

.....but : compromise « ceramic yield / processing properties »



Borazine (I) Polymers with high ceramic yield and low processability

Liquid/Vapor or Liquid/Solid state process



2,4,6-tri(methylamino)borazine (s)

Polymers with lower ceramic yield and good processability

Molten state/solution

Boron nitride fibers : Polymer melt-spinning



Boron nitride fibers : Polymer melt-spinning

Module de Young, E (GPa)



Fibres BN dérivées de (NHMe)₃B₃N₃H₃



Surface lisse
 Structure granulaire
 fibre polycristalline

Tensile strength: 1460 MPa Young modulus: 400 GPa Diameter: 7.5 μm





Boron nitride ordered mesoporous powder

→ Mesoporous materials : high specific surface area, narrow pore size distribution

→ Applications: Catalysis, separation, nanoreactor,...

Synthesis : soft template \longrightarrow (siliceous mesoporous materials)

Non-siliceous mesoporous materials :

Replication of nanoscale structures by direct templating process

→ Hard - template



A. Walcarius. Chem. Soc. Rev., 2013, **42**, 4098-4140

2 to 50 nm

Refractory mesostructured nanoporous materials : BN, SiBCN

Silica template : SBA-15 (hexagonal)

Carbon template : CMK-3 (hexagonal)

KIT-6 (cubic)

CMK-8 (cubic)

Porous boron nitride : *Nanocasting*

ORDERED MESOPOROUS BORON NITRIDE VIA "HEXAGONAL CARBON" TEMPLATING (CMK-3) BN-ex CMK-3

TEM



- Ordering of the porous structure providing by the carbon template preserved
- Centers of the channels distant of ~ 7 nm in agreement with the SA-XRD

Efficiency of the template elimination process

Retention of a porous BN structure

Borazine-derived boron nitride : Liquid/solid-state process



Boron nitride : *Liquid/solid-state process*

Borazine -> Polyborazylene -> BN



Hierarchically porous boron nitride: Hard templating



Boron nitride foam

J. G. Alauzun, S. Ungureanu, N. Brun, S. Bernard, P. Miele, R. Backov, C. Sanchez, *J. Mater. Chem.* 2011, **21**, 14025. * High Internal Phase Emulsion Process Adv. Funct. Mater. 2009, 19, 3136–3145, **R.** Backov *et al.*

CRPP UPR 8641 Université de Bordeaux

BNTi nanocomposites: Nanostructure

Polytitanoborazine → Generation (after pyrolysis) of compounds with low miscibility



SiBCN fibers : Polymer melt-spinning

1st generation of SiBCN fibers by the PDCs route

Melt-spinning







Green Fibers

Curing : 200°C in $NH_3 \neq$ Pyrolysis : 1000°C in N_2



- <u>Curing treatment @ 200°C in NH₃</u>
 ◆ Crosslinking degree of polymer increased
 ◆ Fiber cohesion kept during further pyrolysis
 ◆ Ceramic yield upon pyrolysis increased
 <u>Pyrolysis @ 1000°C in N₂</u>
- S. Bernard, W. Weinmann, D. Cornu, P. Miele, F. Aldinger. J.
 Europ. Ceram. Soc. (2005) 25, 251-256.
 S. Bernard, M. Weinmann, P. Gerstel, P. Miele, F. Aldinger, J.
 Mater. Chem. (2005) 15, 289-299.



Final Ceramic Fibers

SiBCN fibers : Polymer melt-spinning

1st generation of SiBCN fibers by the PDCs route



Nanostuctured porous SiBCN : Nanocasting

"HEXAGONAL" MESOPOROUS SIBCN VIA CMK-3 TEMPLATING



TEM



Catalytic SiC membranes : Dip-coating



Precursors Derived Ceramics et chimie du solide



Collaborations/contacts/réseau

<u>France :</u>

LCTS UMR5801, Bordeaux

LCMCP UMR7574, Paris 6

IS2M UMR7228, Mulhouse

CIRIMAT UMR5085, Toulouse

SPCTS UMR7315, Limoges

IPR UMR6251, Rennes

CRISMAT UMR6508, Caen



Germany : Technische Universität Darmstadt, Universität Bayreuth

<u>Italy</u>: Universita di Trento (Trento), Universita di Padova

Slovakia: Slovak Academy of Sciences (Bratislava)

Sweden : Stockholm University

Japan : Waseda University (Tokyo); Nagoya Institute of Technology (Nagoya)

USA : Clemson University (Clemson)

Brasil : Federal University of Santa Catarina (Florianopolis)

India : Indian Institute of Technology (Madras)

Atomic Layer Deposition : Interest

4 Home-made ALD setups (LTALD, HTALD and PEALD)



Atomic Layer Deposition : *Membranes applications*



Atomic Layer Deposition : *Membranes applications*



Nanoscale 2013 5 9582

Nanotechnology 2015 26 144001

Water desalination



J. Phys. Chem. C 2013 **117** 15306 *Chem. Comm.* 2015 **51** 5994

Confinement of MOFs for membranes preparation

• COUPLING "ALD" AND "SOLVOTHERMAL CONVERSION"



Gas selective membrane with high mechanical and thermal stability

M. Drobek, M. Bechelany et al., Journal of Membrane Science 475 (2015) 39–46

Atomic Layer Deposition : Other applications

Optical (Bio)Sensing



J. Phys. Chem. C 2014 118 3811

J. Mater. Chem. C 2015 3 6815

Photovoltaïc





Nano Energy 2012 1 696

UV & Gas sensing



J. Mater. Chem. A 2014 **2** 20650 *Nanotechnology* 2015 **26** 105501

MOF conversion



Nanoscale 2015 **7** 5794 *J. Membr. Sci.* 2015 **475** 39

Collaborations/contacts/réseau



Acknowledgments

Boron Nitride Ceramics from Molecular Precursor: Synthesis, **Properties and Applications**

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Samuel Bernard, Chrystelle Salameh[†] and Philippe Miele*

DOI: 10.1039/x0xx00000x

Transactions

Dalton



Adv. Mater. 2012, 24, 1017-1032

ADVANCED vww.advmat.de

www.MaterialsViews.com



Atomic Layer Deposition of Nanostructured Materials for Energy and Environmental Applications

Catherine Marichy, Mikhael Bechelany, and Nicola Pinna*



Dr. Samuel BERNARD Dr. Mikhael BECHELANY Dr. Bernard BONNETOT Prof. David CORNU Dr. Bérangère TOURY + nombreux thésards



Boron nitride fibers : *Polymer melt-spinning*

MELT-SPINNABILITY OF POLY(METHYLAMINO)BORAZINE



Stretching Rupture



Viscoelastic behavior (shear rheometry)



b good spinnability at medium rate fiber rupture at high rate

200 *µ*m

smooth, defect-free green fibers

high-performance BN fibers







Tensile strength: 1460 MPa

Young modulus: 400 GPa

Diameter: 7.5 µm

Nanostuctured porous SiAICN : Nanocasting



•First thermal treatment: under N₂ at 1000°C for the ceramic conversion

•Second thermal treatment: under NH₃ at 1000°C for the template removal

Atomic Layer Deposition : Membranes applications



Nanoscale 2013 5 9582

Nanotechnology 2015 26 144001

Gas barrier



Paper in preparation



Cl

Water desalination

mic layer depose HMDS coating

