



U.S. DEPARTMENT OF
ENERGY

PNNL-22370

Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Composite Synthesis Methodology Development

Nanocrystalline SiC and Ti_3SiC_2 Alloys for Reactor Materials

Outline of Initial Synthesis Capabilities

M4CT-13PN0405034

CH Henager, Jr. (PI)
KJ Alvine
Y Shin
W Jiang
BN Nguyen

March 28, 2013



Pacific Northwest
NATIONAL LABORATORY

*Proudly Operated by **Battelle** Since 1965*

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor Battelle Memorial Institute, nor any of their employees, makes **any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.** Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or Battelle Memorial Institute. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

PACIFIC NORTHWEST NATIONAL LABORATORY

operated by

BATTELLE

for the

UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161
ph: (800) 553-6847
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: <http://www.ntis.gov/ordering.htm>



This document was printed on recycled paper.

(9/2003)

Nanocrystalline SiC and Ti₃SiC₂ Alloys for Reactor Materials

Outline of initial synthesis capabilities

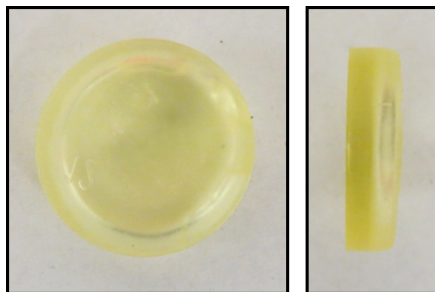
M4CT-13PN0405034

Composite Synthesis Methodology Development

Introduction

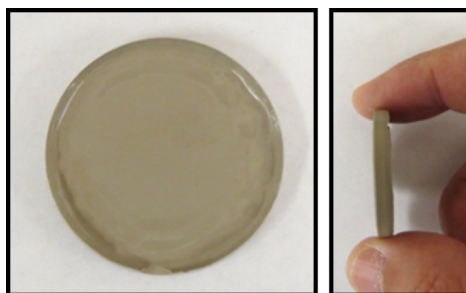
This is an interim letter report outlining the status of our initial synthesis progress for the NEET project on SiC-based alloys for advanced reactor materials.

1. We have identified three initial preceramic polymers to help produce the SiC-based alloys for this project and have developed simple processing steps to make SiC-based alloy ceramics. The use of unfilled SMP-10 (Polycarbosilane) or SMP-877 (Methyl-Polycarbosilane) is not feasible due to the large mass losses that occur during pyrolysis. The pre-gelling steps below save time when those two polymers are filled with powders. The use of SL-MS30 provides us with a SiC-filled polymer that can be used to test out the CNT mats without further complications due to other powders.
 - a. Starfire SMP-10 – Polycarbosilane: Green curing of SMP-10 is achieved in a plastic mold for 7-10 days at 323 K. At these low temperatures an inert atmosphere (nitrogen or argon) and vacuum are not required. We conducted this work in a simple air-convection oven. Such slow sol-gel processing releases hydrogen and the polymer cures in 7 days. We also use pre-gelled SMP-10 (1-2 h heating at 323 K upon stirring) that takes 5 days to cure.
 - b. Starfire SMP-877 – Polycarbosilane with excess Carbon in the form of methyl groups: Green curing of SMP-877 is achieved in a plastic mold for 14-16 days at 323 K because the hydrogen in SMP-10 is replaced with a methyl group. At low temperatures an inert atmosphere (nitrogen or argon) and vacuum are not required. We conducted this work in a simple air-convection oven. We also use pre-gelled SMP-877 (3-4 h heating at 323 K upon stirring) that takes 5 days to cure.



1-inch molded disk of SMP-877

- c. Starfire SL-MS30 – SiC-powder-filled Polycarbosilane: Unlike SMP-10 and SMP-877, SL-MS30 does not need a pre-gelling process because it contains SiC filler powders. It does not show severe volume contraction during the molding process and cures in 5 days at 323 K.



1-inch molded disk of SL-MS30.

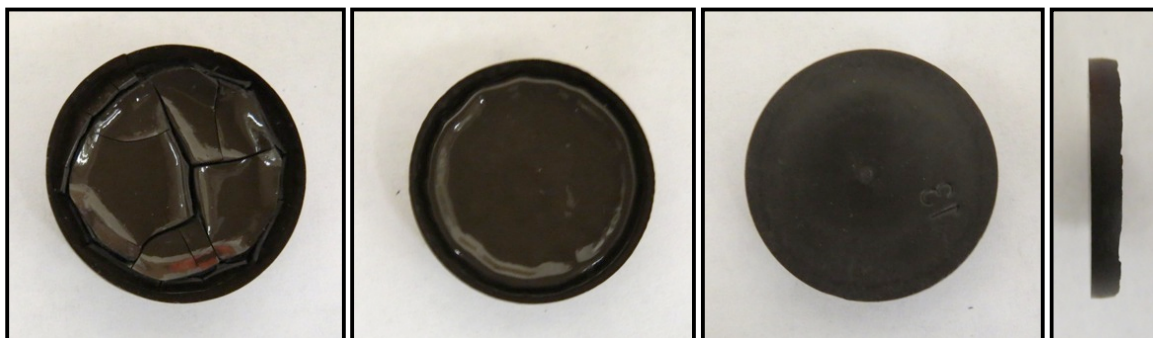
Nanocrystalline SiC and Ti₃SiC₂ Alloys for Reactor Materials

Outline of initial synthesis capabilities

M4CT-13PN0405034

2. We have initially prepared two types of fillers for these polymers in addition to the SiC-powder filler in the SL-MS30.
 - a. Preblended TiC+Si powders in a 3:2 ratio of TiC:Si. TiC + Si (31.98 g TiC + 10 g Si in a 3:2 molar ratio; TiC: 2 μ m, 99.5% from Alfa Aesar; Si: 10 μ m, 98% from Cerac Chemical) The powder mixture is ball-milled for 8 h with zirconia balls.
 - b. Carbon nanotube (CNT) materials are multi-wall carbon nanotubes 20-30 nm in diameter. CNT are purchased from “cheaptubes” and come in either NH₂ functionalized or non-functionalized forms. CNTs are manually stirred into the polymeric materials at specified loadings. After mixing, the solution is degassed for several hours to remove air incorporated during the mixing step. An optional high-powered sonication step is also used for a higher degree of homogenization. These CNTs can also be dispersed via sonication into a variety of solvents for handling.
3. SMP-10 – Pure Polycarbosilane with fillers.
 - a. This polymer can be readily cured to produce a solid green ceramic by filling with at least 50% by volume of blended TiC+Si powders, up to 80% solids loading by weight.
 - i. TiC + Si (31.98 g TiC + 10 g Si as a 3:2 molar ratio) mixture was ball-milled for 8 h. Pre-gelled SMP-10 polymer was added to the powder mixture and ball-milled for 16 h. The ball-milled mixtures were thickened to have higher viscosity (~20,000cp) upon heating at 323 K for 2-12 h. The powder loading was 50-80% by weight. The mixtures were cured after 8 days in air at 323 K.

Sample (solid loading, %)	TiC (g)	Si (g)	SMP-10 (g)	Ball-milling time (h) before adding polymer	Ball-milling time (h) after adding polymer	Aging time before starting molding (h)	Molding time (d)
50	31.98	10	42	8	16	12	8
60	31.98	10	28	8	16	10	8
70	31.98	10	18	8	16	6	8
75	31.98	10	14	8	16	3	7
80	31.98	10	10.5	8	16	2	7



1-inch molded disks of SMP-10 with 50% powder loading as described above.

Nanocrystalline SiC and Ti₃SiC₂ Alloys for Reactor Materials

Outline of initial synthesis capabilities

M4CT-13PN0405034

- b. CNTs are manually stirred into the SMP-10 at up to 15% loading by weight. Beyond these loadings, the solution becomes solid and no longer flows making high quality samples difficult to achieve. After mixing, the solution is degassed for several hours to remove air incorporated during the mixing step. The solutions are then poured into 2-part delrin molds and baked in air at 358 K for 3-5 days followed by a higher temperature cure at 398 K overnight to completely solidify the material.
4. SMP-877 – Carbon-rich Polycarbosilane with filler powders
 - a. This polymer can be prepared into a stable gel by curing at 323 K and can be molded into a solid green ceramic by loading with at least 25% blended TiC+Si powders, up to 80% solids loading by weight.
 - i. TiC + Si (31.98 g TiC + 10 g Si as a 3:2 molar ratio) mixture was ball-milled for 8 h. Pre-gelled SMP-877 polymer was added to the powder mixture and ball-milled for 16 h. The ball-milled mixtures were thickened to have higher viscosity (1,000-4,000cp) upon heating at 323 K for 4-20 hours. The powder loading was 50-80% by weight. The mixtures were cured after 8 days in air at 323 K.

Sample (solid loading, %)	TiC (g)	Si (g)	SMP-877 (g)	Ball-milling time (h) before adding polymer	Ball-milling time (h) after adding polymer	Aging time before starting molding (h)	Molding time (d)
50	31.98	10	42	8	16	20	9
60	31.98	10	28	8	16	20	9
70	31.98	10	18	8	16	16	8
75	31.98	10	14	8	16	4	8
80	31.98	10	10.5	8	16	4	8



1-inch molded disks of SMP-877 with 75% powder loading as described above.

- b. CNTs are manually stirred into the SMP-877 at up to 15% loading by weight. Beyond these loadings, the solution becomes solid like and no longer flows making high quality samples difficult to achieve. After mixing, the solution is degassed for several hours to remove air incorporated during the mixing step. The solutions are then poured into 2-part delrin molds and baked in air at 358 K for 3-5 days followed by a higher temperature cure at 398 K overnight to completely solidify the material.

Nanocrystalline SiC and Ti₃SiC₂ Alloys for Reactor Materials

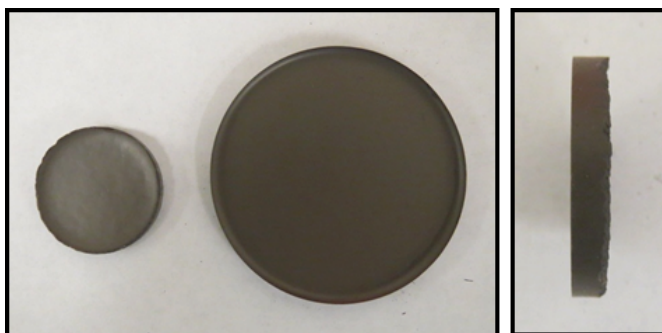
Outline of initial synthesis capabilities

M4CT-13PN0405034

5. SL-MS30 – SiC-filled Polycarbosilane

- a. This is by far the easiest of the polymers to work with. It is readily cured at 323 K for 12 h in air without any additional powder loading. This polymer can be filled up to 60% total loading by weight via adding additional TiC+Si powders via ball-mixing and then curing at 323 K for 12 hours in air. TiC + Si (15.99 g TiC + 5.00 g Si as a 3:2 molar ratio) mixture was ball-milled for 8 h. SL-MS30 (weight ratio of solid loading: 60%) was added to the powder mixture and ball-milled for 16 h. Since TiC has much higher density (4.39 g/cm³) than the polymers (1.0 g/cm³) and Si (2.33 g/cm³), it is important to maintain high viscosities during the molding process. It is also important to mill right before putting the materials in the mold even though the mixtures were previously milled. It takes 4 to 5 days to cure under these conditions.

Sample (solid loading, %)	TiC (g)	Si (g)	SL-MS30 (g)	Ball-milling time (h) before adding polymer	Ball-milling time (h) after adding polymer	Aging time before starting molding (h)	Molding time (d)
20	15.99	5	84	8	16	0	5
30	15.99	5	49	8	16	0	5
40	15.99	5	31.5	8	16	0	5
50	15.99	5	21	8	16	0	4
60	15.99	5	14	8	16	0	3



1-inch and 2-inch disks molded from 60% powder loaded SL-MS30.

- b. CNTs are manually stirred into the SL-MS30 at up to 5% loading by weight. Beyond these loadings, the solution becomes solid like and no longer flows making high quality samples difficult to achieve. After mixing, the solution is degassed for several hours to remove air incorporated during the mixing step. The solutions are then poured into 2-part delrin molds and baked in air at 358 K for 3-5 days followed by a higher temperature cure at 398 K overnight to completely solidify the material. The SL-MS30/CNT samples contain higher total solids loading and solidify more quickly than do the SMP-10/877 materials with added CNTs.

Nanocrystalline SiC and Ti₃SiC₂ Alloys for Reactor Materials

Outline of initial synthesis capabilities

M4CT-13PN0405034

6. Conclusions and summary of synthesis capabilities for producing SiC-based alloys.
 - a. We have identified three different preceramic polymers that can be used to provide powder slurries that will produce SiC-based alloys and that can also contain up to 15% by weight of CNTs. The CNT loading can be increased through a process of pyrolysis and re-infiltration but that process is not described here since it is currently still under development at our lab.
 - b. The polymers can be pre-gelled by curing in air at 323 K for several days.
 - c. Both SMP-10 and SMP-877 can be loaded up to about 80% solids loading using blended TiC+Si powders to achieve a filled preceramic polymer system that will form the backbone of the SiC-based alloys for the remainder of this project.
 - d. The SL-MS30 polymer can be filled up to 60% by weight of TiC+Si powders since the polymer already contains some SiC-filler powders.
 - e. These powder-filled polymers can then be cured into stable green disks via a molding and curing process that depends on the type of polymer and on the solids loading.
 - f. CNTs can also be added up to 5% to 15% by weight to these polymers and cured.
 - g. We still have to demonstrate a combined CNT and powder-filled polymer other than having added CNTs to the SL-MS30 SiC-filled polymer but we know that we can do that.
 - h. These green cured disks can be further processed by hot-pressing and sintering to achieve SiC-based alloys with improved properties but that portion of the work is still under development at our lab.