第56回高分子討論会

超高分子量PCSを用いる先進PIP法による SiC/SiCの緻密化

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原子力機構　田口 富嗣

目的

- 原子力関連材料：燃料被覆管、核融合炉用構造材料
- 宇宙材料：セラミックス系スラスタ、熱防御システム
- 対環境材料：超耐酸化性炭素系複合材料
- 耐熱構造材料：自動車関連材料

従来のCMC製造方法	*繊維へのﾀﾞﾒｰｼﾞ*	*純度*	*気孔率*	*コスト*
化学気相浸透法	◎	◎	×	×
反応焼結法	△	○	◎	×
*ホットプレス法 → NITE法**	×→ ◎	×	◎	×
ポリマー含浸焼成法（PIP法）	◎	× → ○	× → ○	◎

** NITE (Nano-powder Infiltration and Transient Eutectic-phase)法*

PIP法の最重要課題：**緻密化**

先進PIP 法

⇩

- *気孔率＜10%で複雑形状に対応できる低コストなSiC/SiCの提供*
- *強度の向上、熱伝導率制御、新インターフェイズの実現*

先進PIP (APIP：Advanced Polymer Infiltration and Pyrolysis)法

APIP法のコンセプト

全ての原料がPCS由来

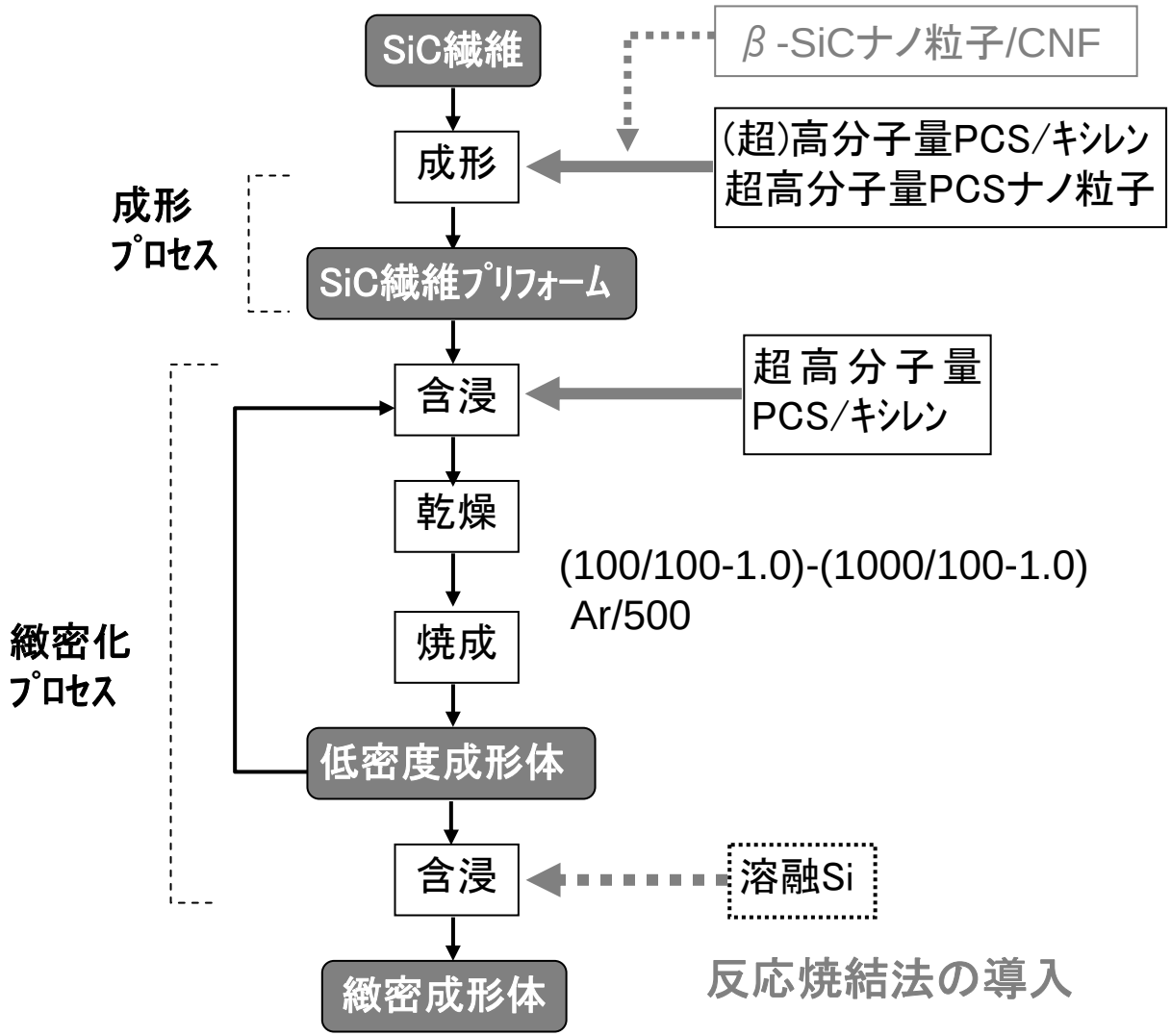
さらに

SiCナノ粒子やCNFの利用による緻密化、高純度化、強度の向上、高熱伝導率化

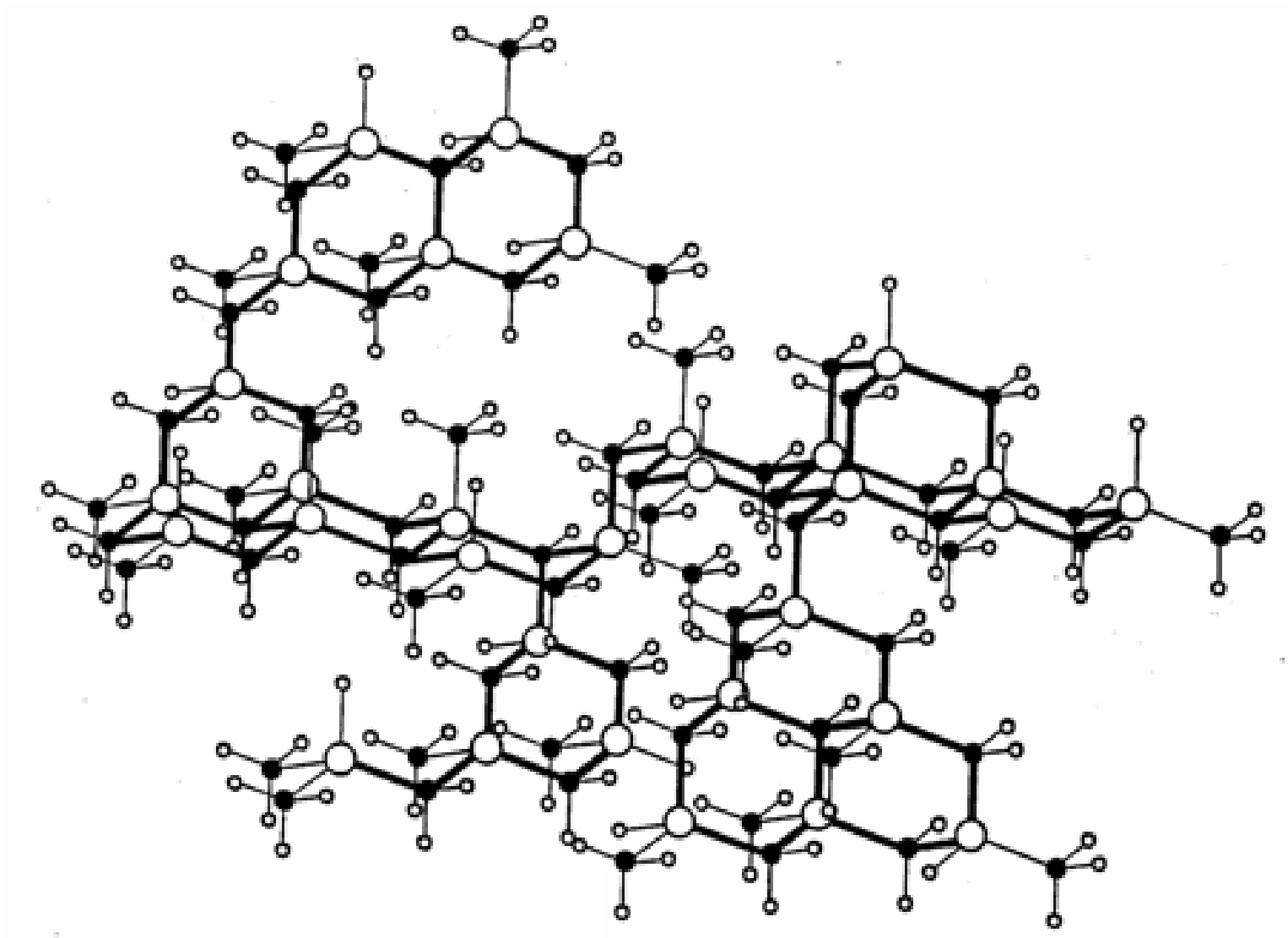
本研究では

- CNFの緻密化効果
- 不融性PCSナノ粒子の自己焼結によるプリォーム形成
- CNF、不融性PCSナノ粒子による新インターフェイズの形成

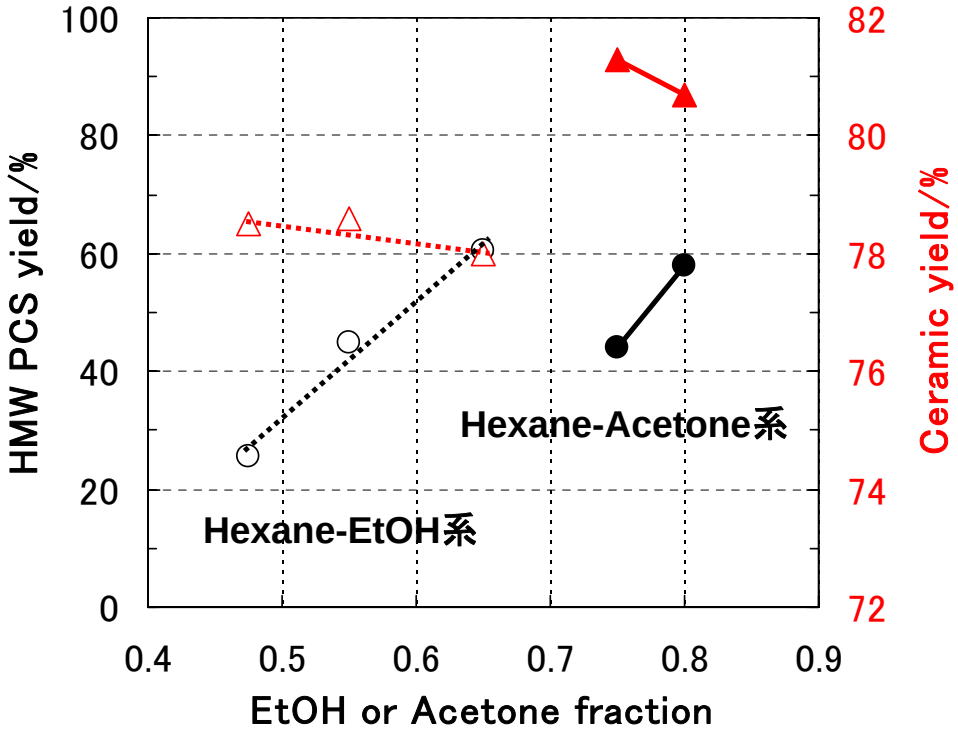
APIP法



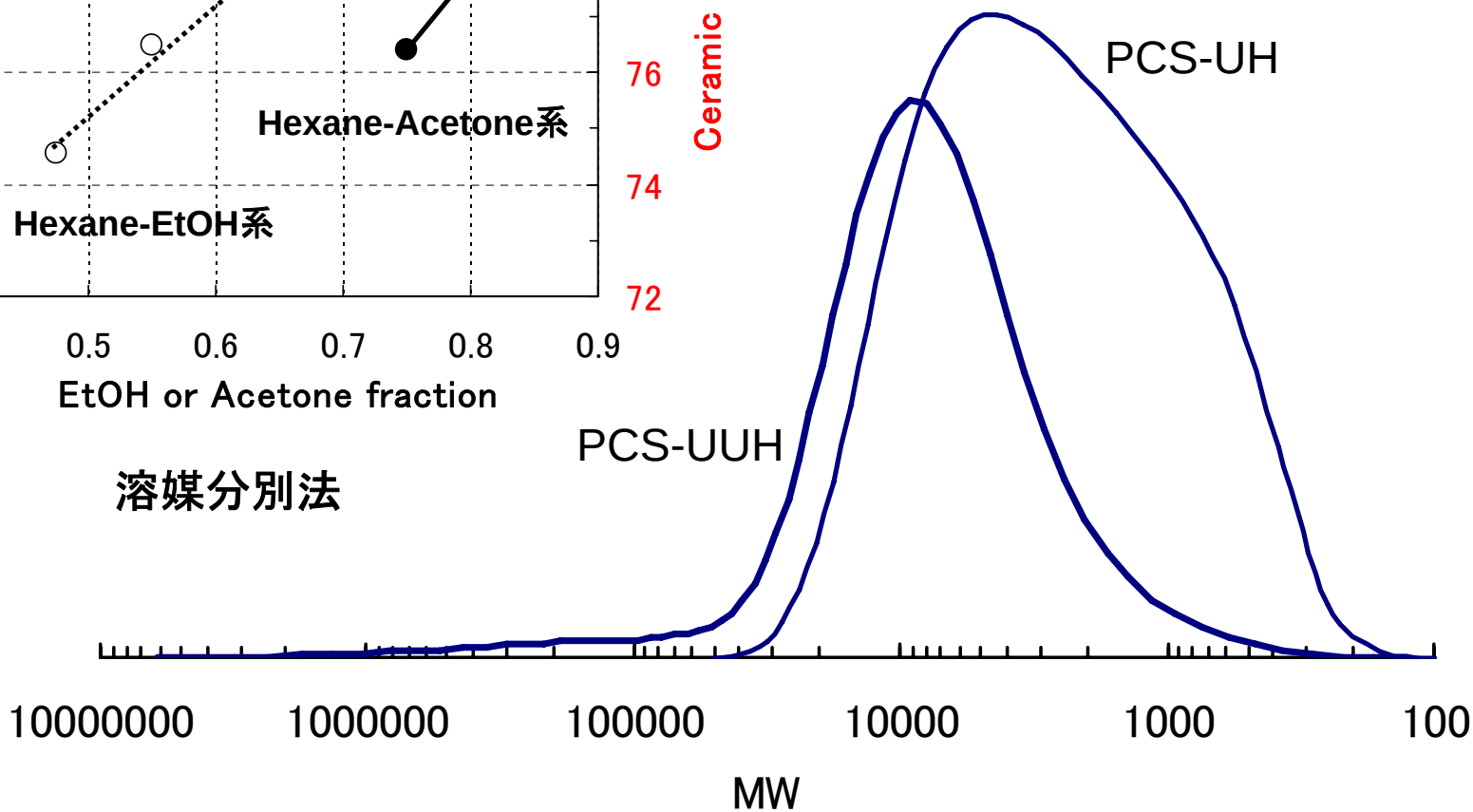
ポリカルボシラン(Polycarbosilane)



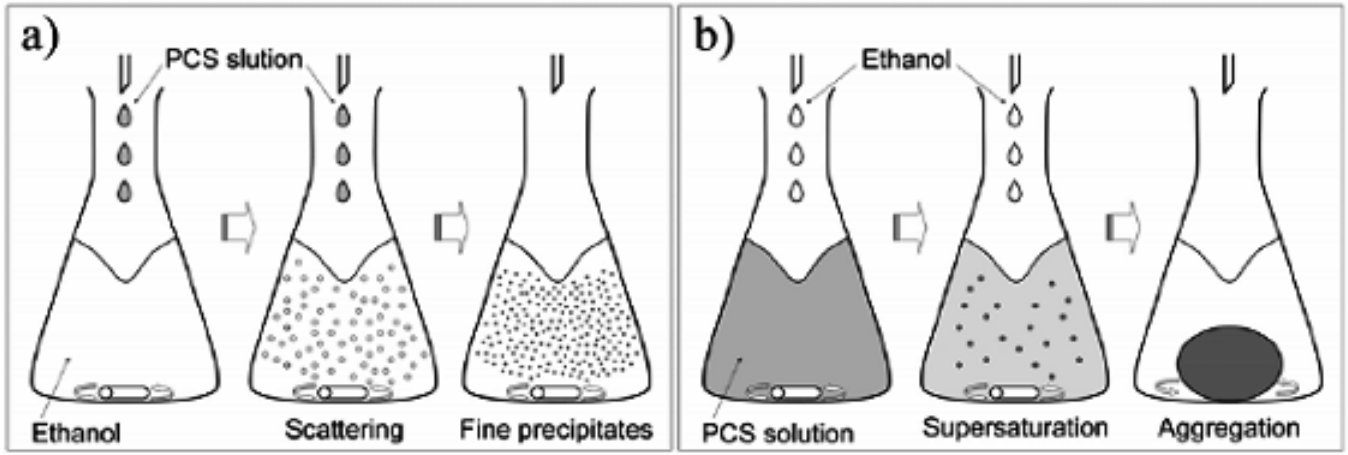
不融性超高分子量ポリカルボシラン(PCS-UUH)の調製



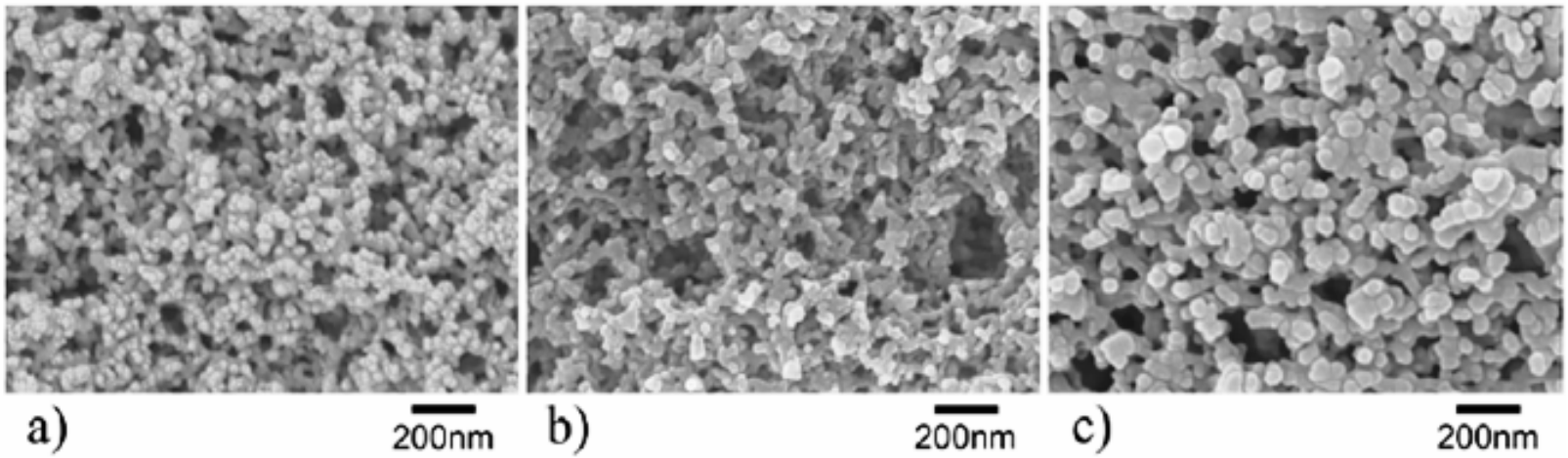
溶媒分別法



PCS-UUHナノ粒子の調製



PCS-UUHナノ粒子の調製法



PCS-UUHナノ粒子　不融化PCS-UUHナノ粒子　1000℃焼成

(S. Ishihara, T. Nishimura, and H. Tanaka, “Fine polycarbosilane particles for precursors of silicon carbide ceramics synthesized by precipitation processing in solvents”, The Fifth World Congress on Particle Technology, 2006)

SiC焼結体(マトリックスSiC)の作製

PCS-derived SiC微粉末
＋
PCS-UH微粉末：10vol%
＋
ステアリン酸：2wt%

100MPa ⇩

ρ :1.55g・cm^{-3}

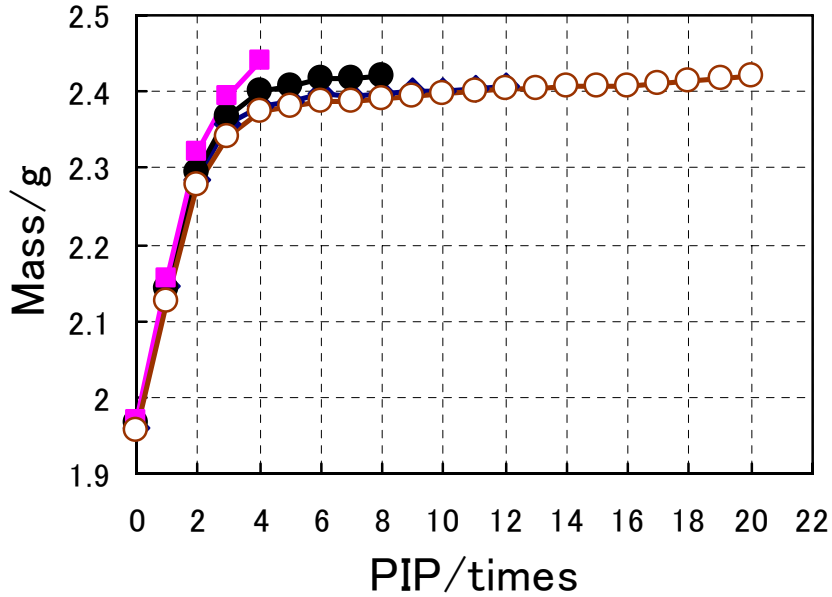
1000/100-1.0, Ar/250 ⇩

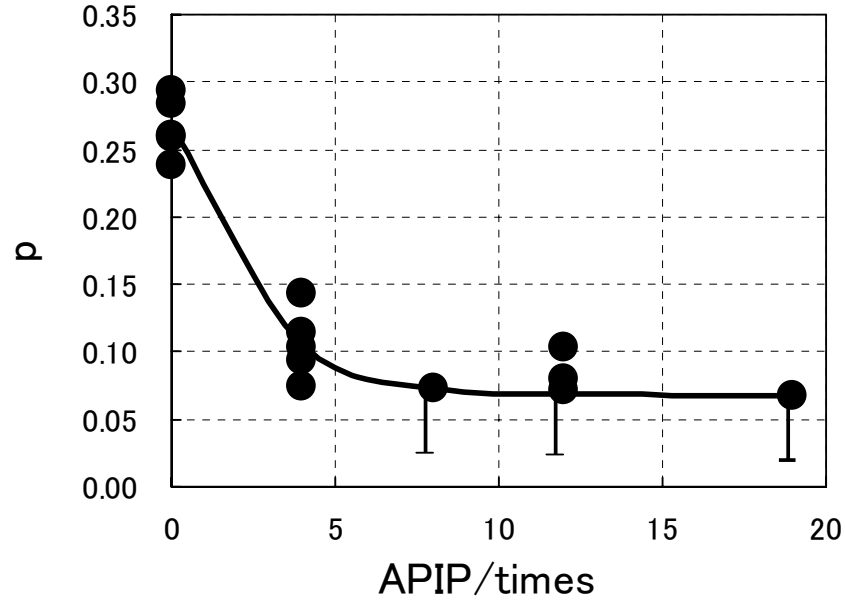
ρ :1.58g・cm^{-3}
収縮率：1.8%

APIP ⇩

SiC/SiCのマトリックス
模擬焼結体

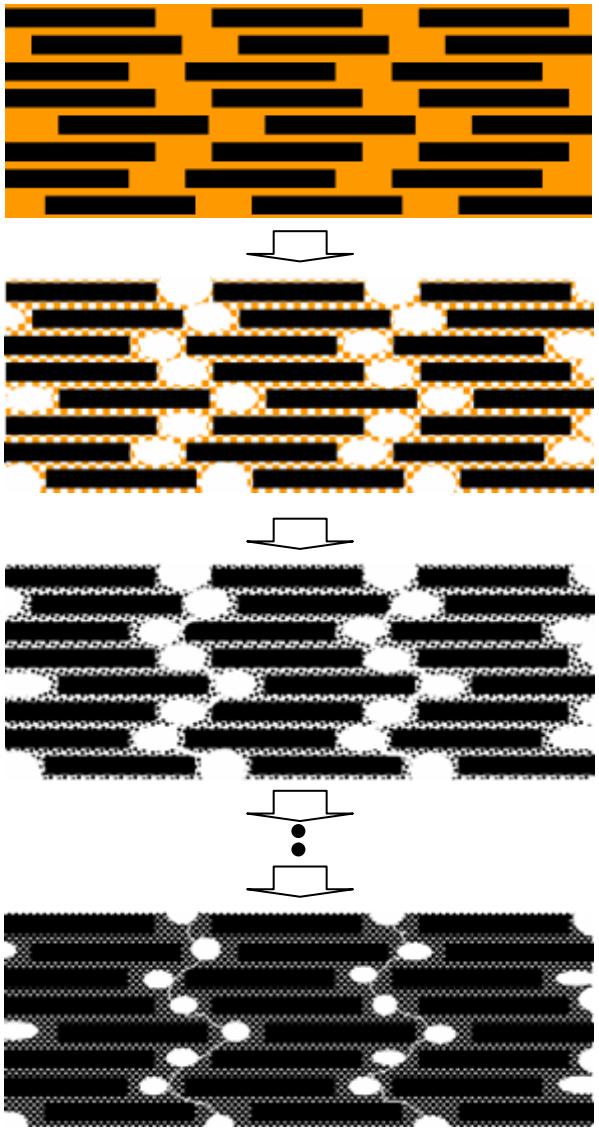
PIP5~6回で p<0.10 達成





SiC/SiC製造プロセス

APIP(T-1)



成型

⇩

乾燥

⇩

グリーンボディ

⇩

焼成

⇩

Porous Composites

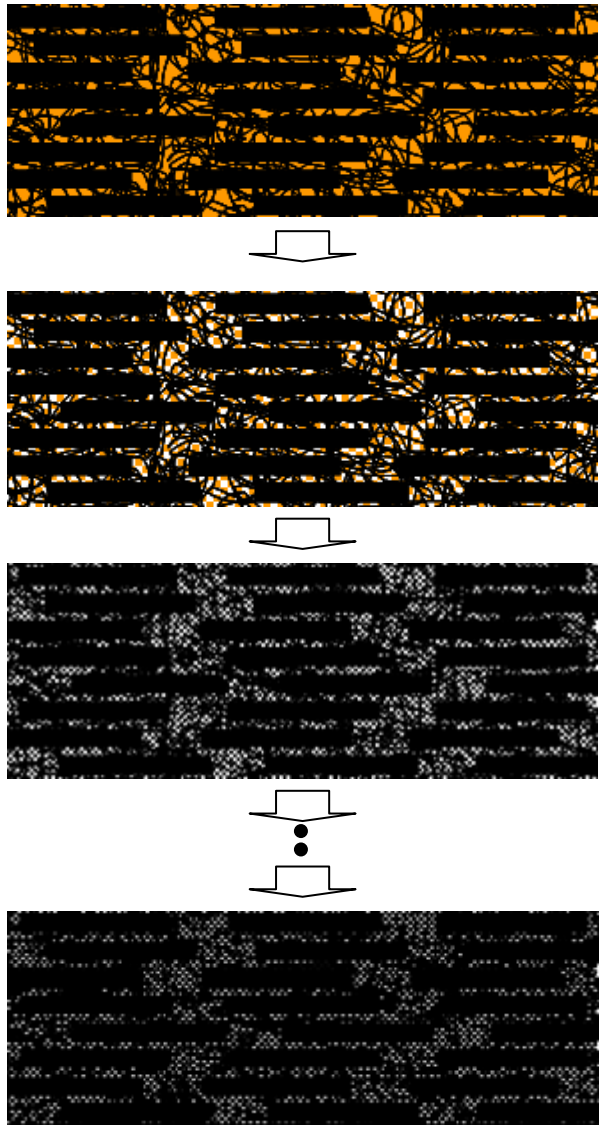
⇩

PIP

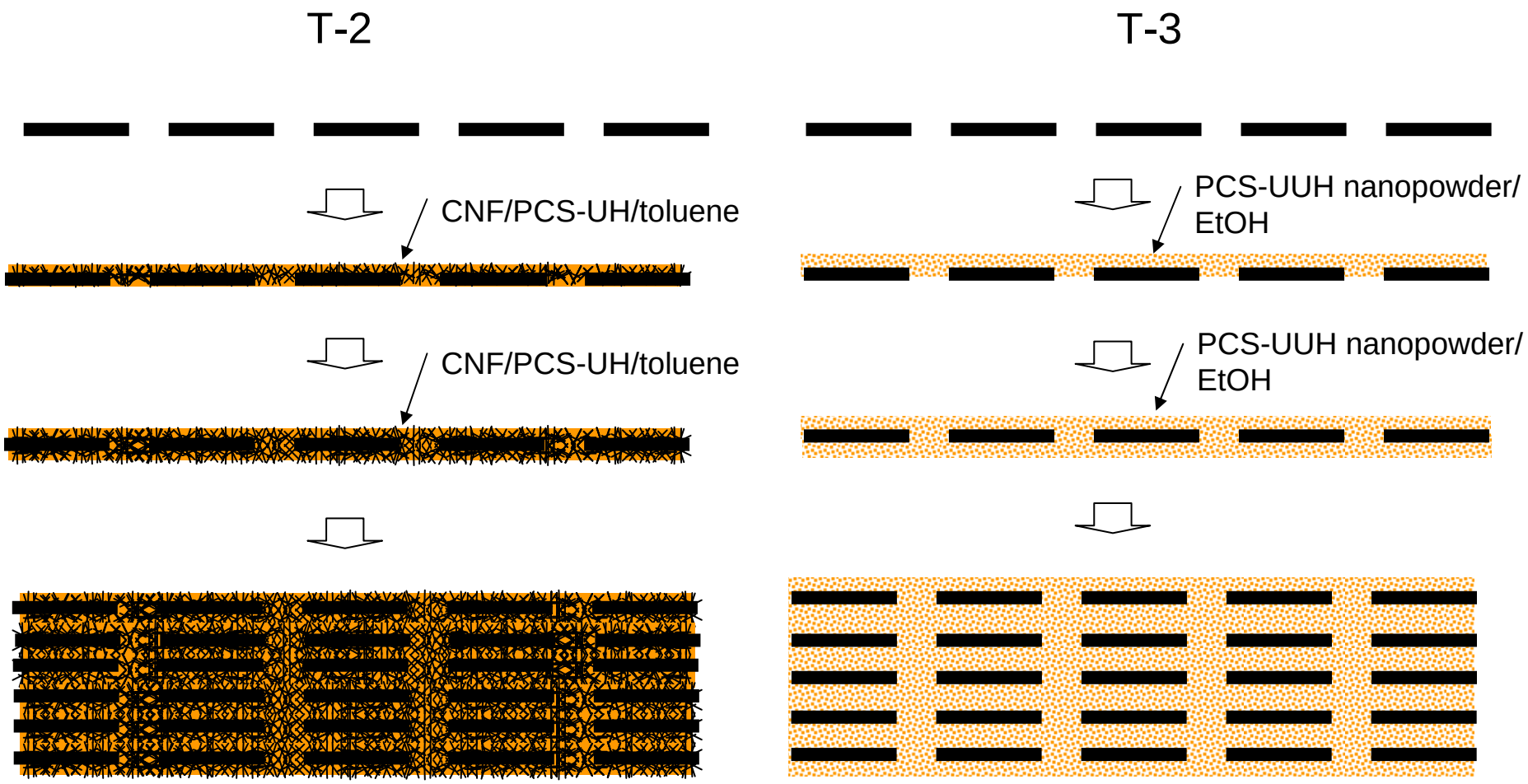
⇩

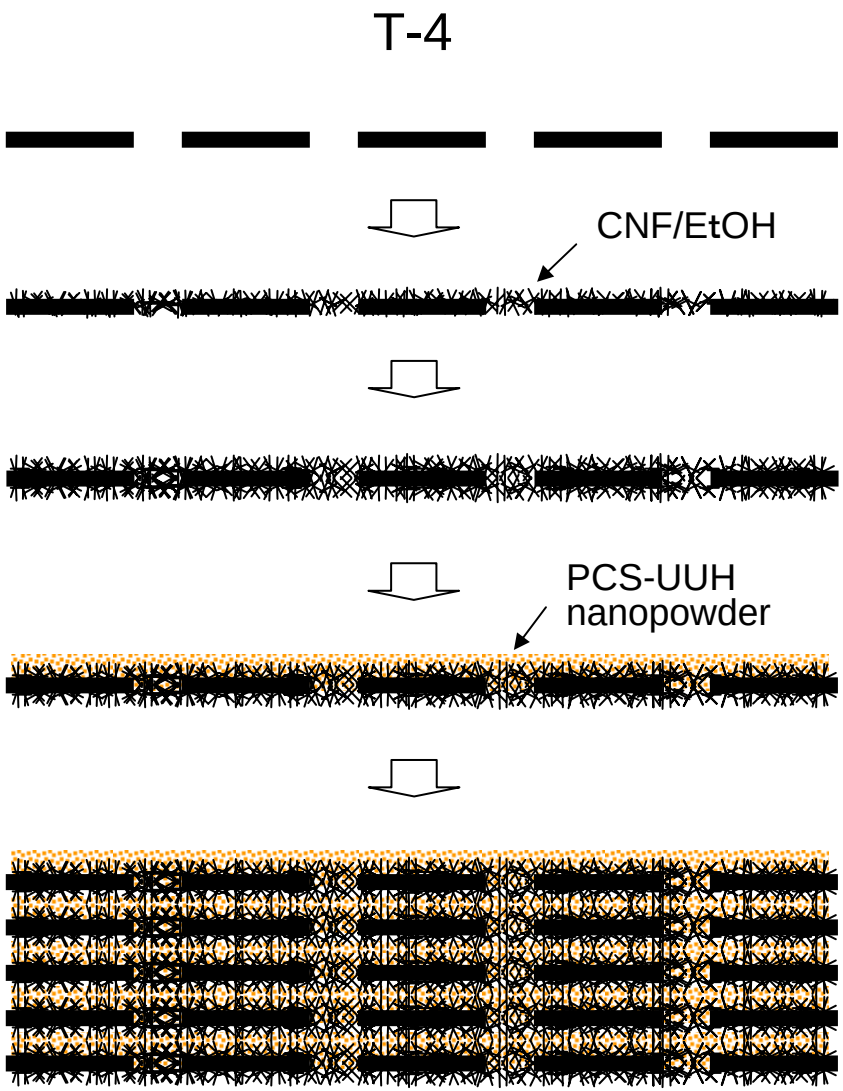
Dense Composites

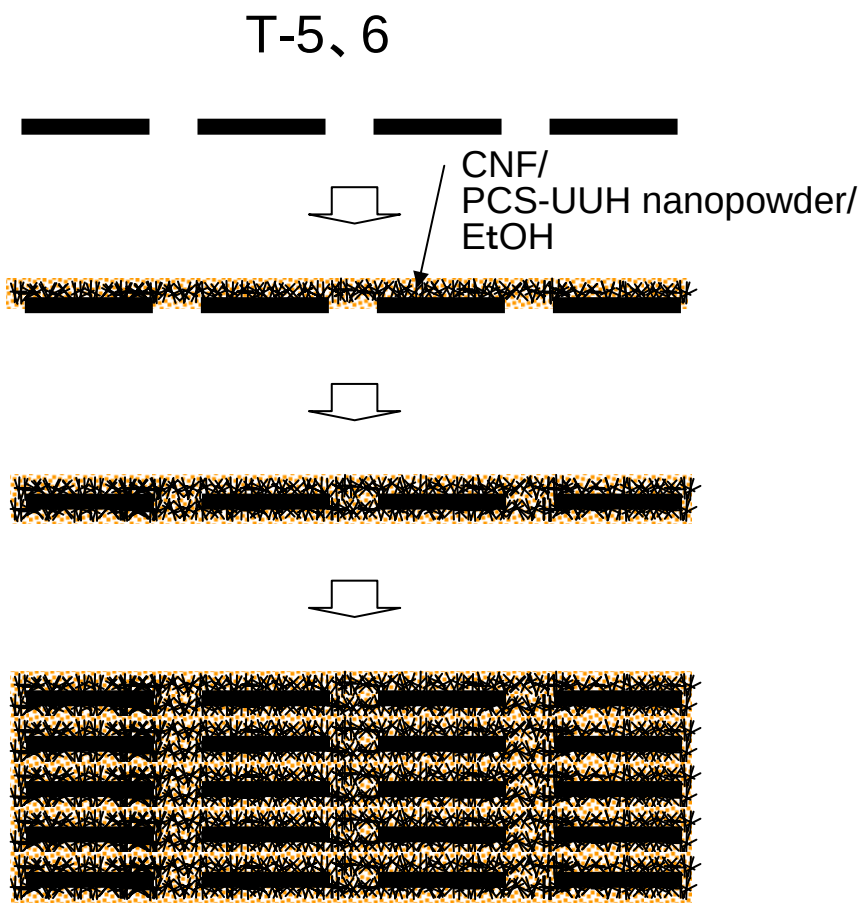
APIP(フィラー成形法)



APIP(フィラー成形法)



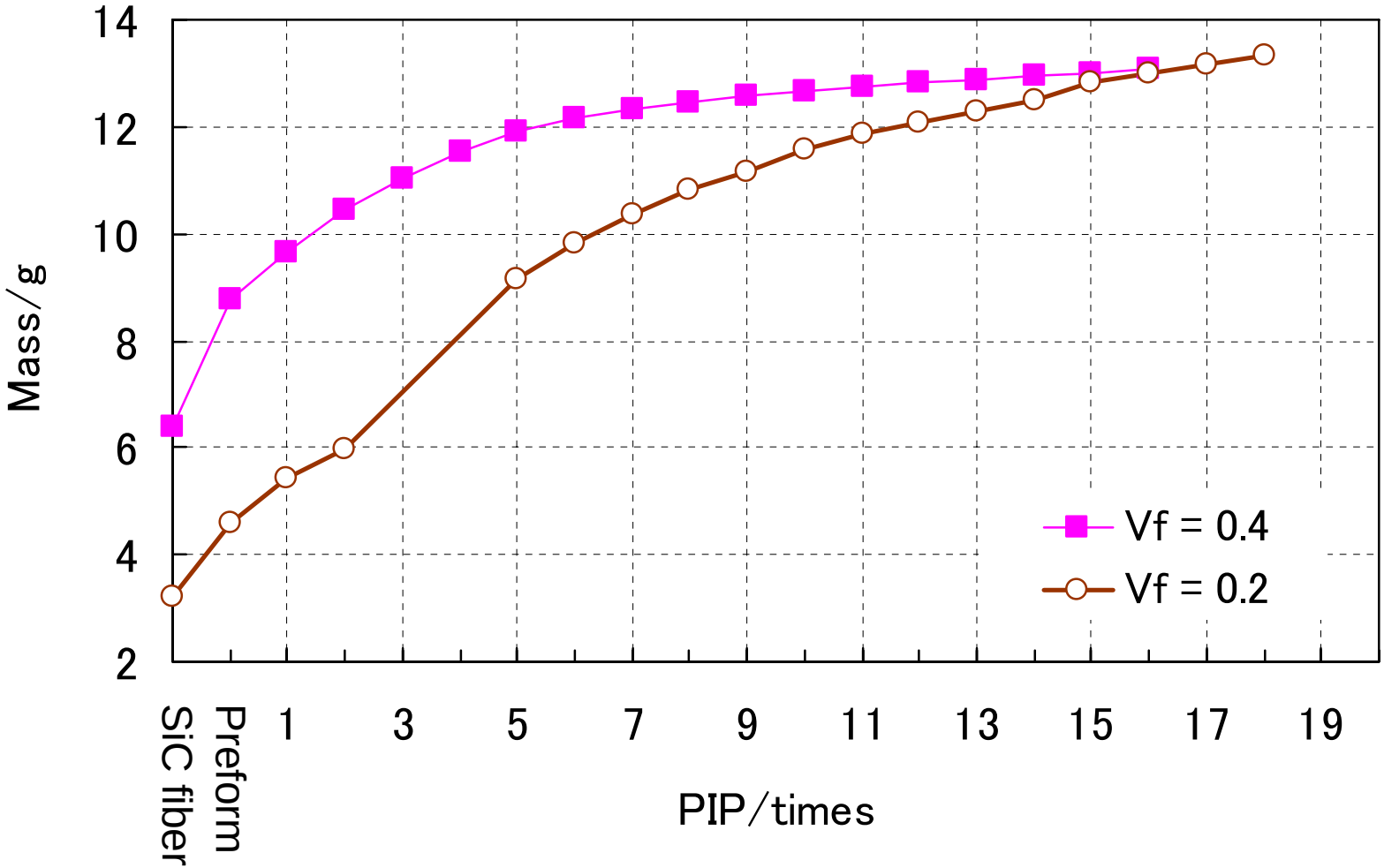

T-4
CNF/EtOH
PCS-UUH
nanopowder


T-5、6
CNF/
PCS-UUH nanopowder/
EtOH

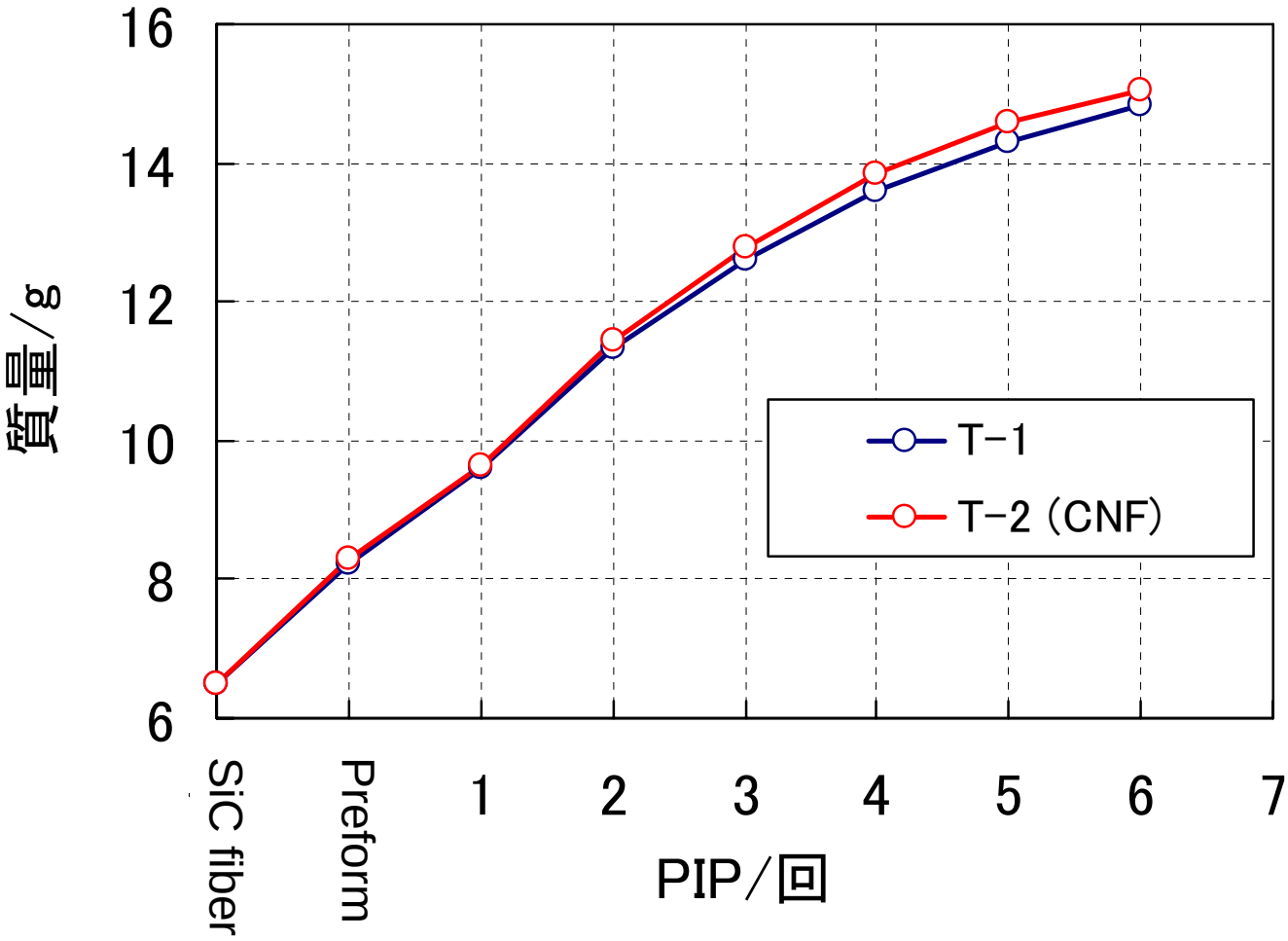
1D、2D-SiC/SiCの特性

<table>
<tr><th rowspan="2">Sample</th><th rowspan="2">SiC fiber</th><th rowspan="2">Binder</th><th colspan="2">APIP</th><th rowspan="2">t/cm</th><th rowspan="2">V_f</th><th rowspan="2">p</th><th rowspan="2">σ/MPa</th><th rowspan="2">備考</th></tr>
<tr><th>PCS</th><th>PIP/times</th></tr>
<tr><td>1D-SiC/SiC
(V_f=0.2)</td><td>HNL</td><td rowspan="3">PCS-UH</td><td rowspan="8">PCS-UUH</td><td>18</td><td>0.126</td><td>0.201</td><td>0.043</td><td>－</td><td></td></tr>
<tr><td>1D-SiC/SiC
(V_f=0.4)</td><td>HNL</td><td>12</td><td>0.122</td><td>0.414</td><td>0.100</td><td>－</td><td></td></tr>
<tr><td rowspan="6">2D-SiC/SiC
(V_f=0.4)</td><td rowspan="2">HNL-S</td><td rowspan="6">6</td><td>0.188</td><td>0.377</td><td>0.132</td><td>448</td><td>T-1</td></tr>
<tr><td>PCS-UH +
CNF</td><td>0.198</td><td>0.377</td><td>0.136</td><td>383</td><td>T-2</td></tr>
<tr><td rowspan="4">HNL</td><td>PCS-UUH
nanopowder</td><td>0.111</td><td>0.404</td><td>0.146</td><td>198</td><td>T-3</td></tr>
<tr><td rowspan="3">PCS-UUH
nanopowder
+
CNF</td><td rowspan="3">~0.1</td><td rowspan="3">~0.4</td><td>0.137</td><td>123</td><td>T-4</td></tr>
<tr><td>0.114</td><td>181</td><td>T-5</td></tr>
<tr><td>0.128</td><td>151</td><td>T-6</td></tr>
</table>

1D-SiC/SiCの作製



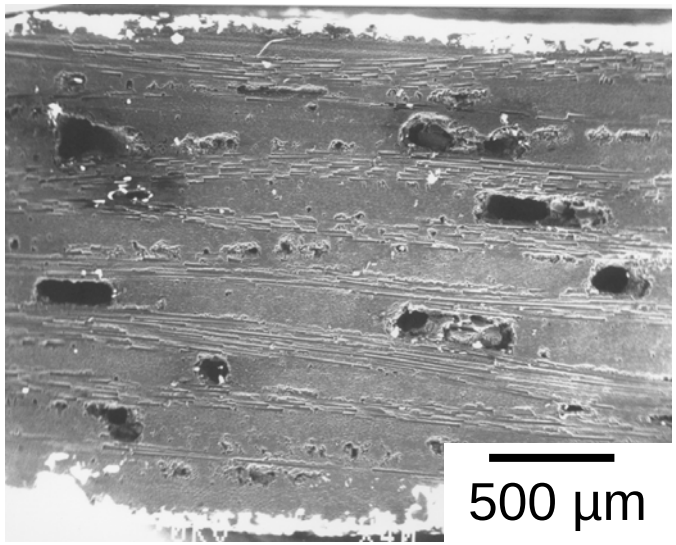
フィラー(CNF)成形法SiC/SiC複合材料の作製



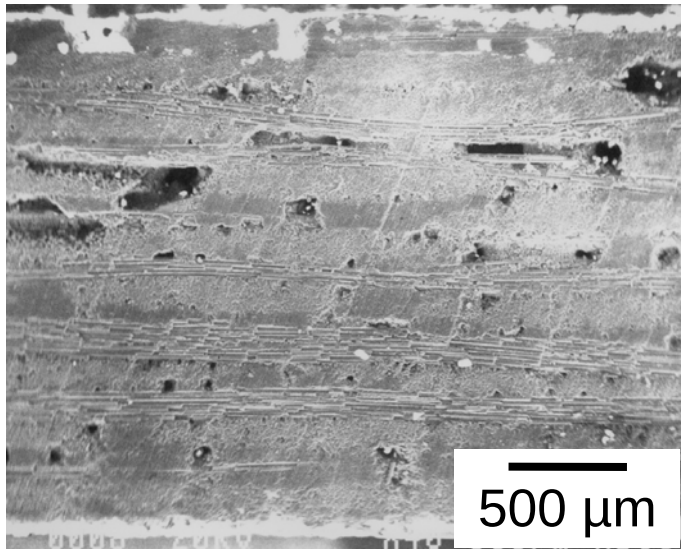
*含浸:PCS−UUH 60% xylene 溶液

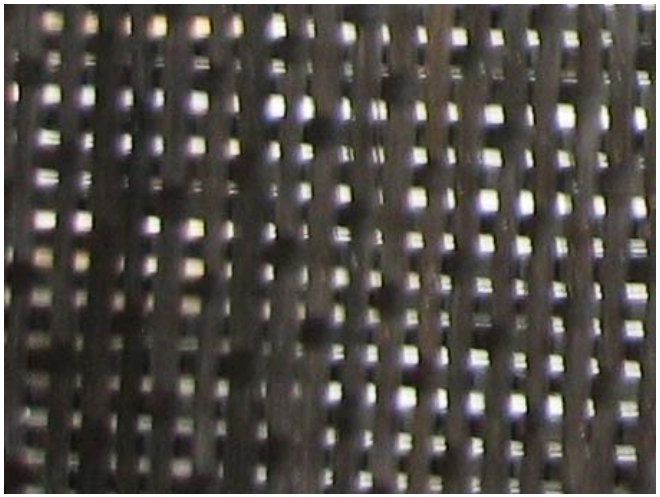
フィラー(CNF)成形法SiC/SiC複合材料の断面SEM観察結果

T-1（CNF無添加）

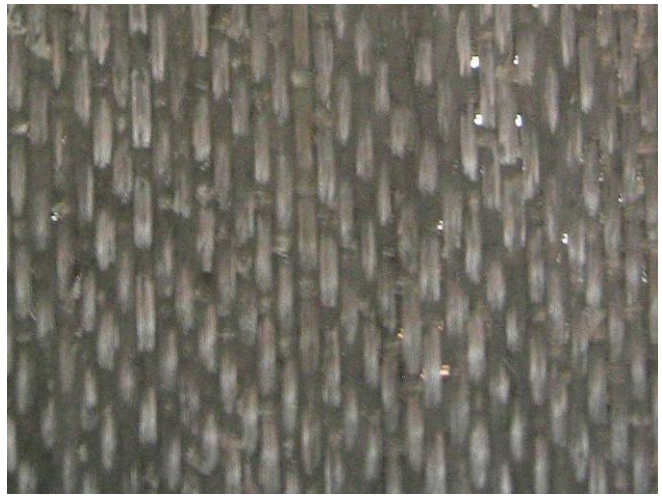


T-2（CNF添加）





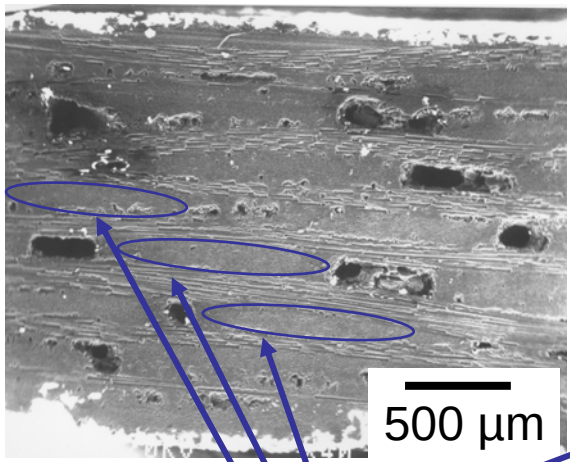
HNL-S5枚朱子織(CNF塗布前)

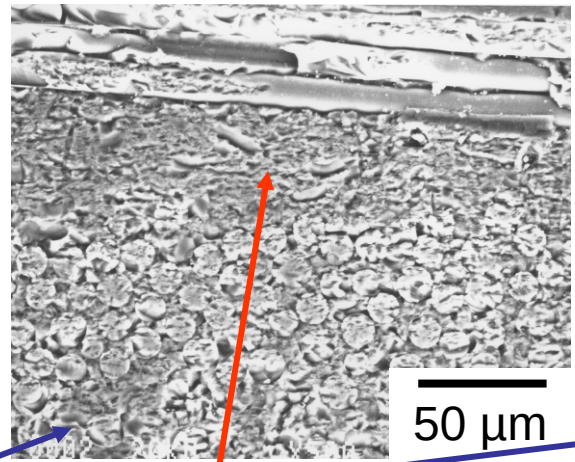


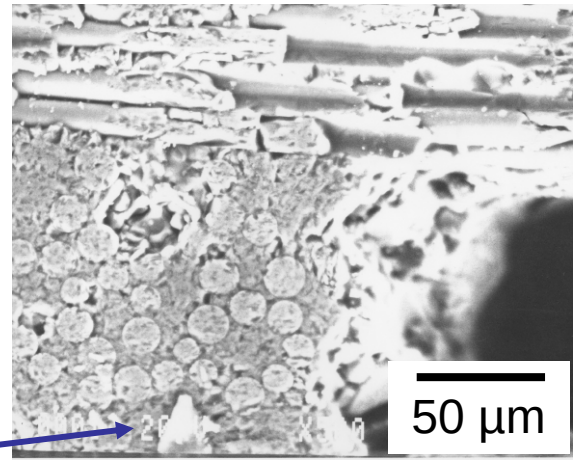
CNF塗布後

T-1（CNF無添加）　SiC繊維束内部及び表面近傍にのみマトリックスが生成

SiC繊維バンドルがない部分は、気孔

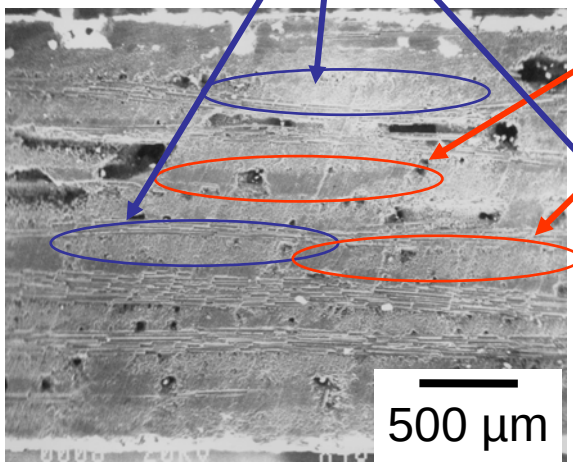


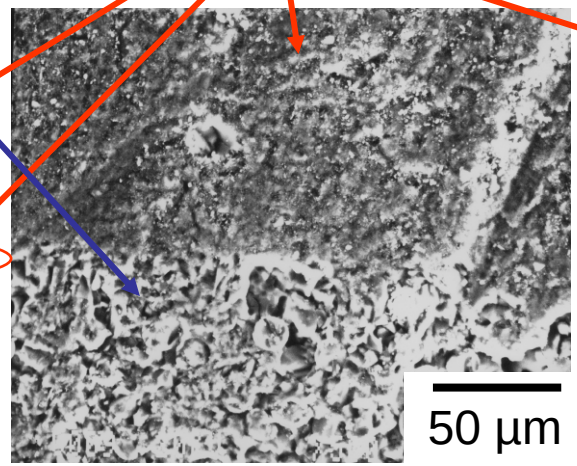


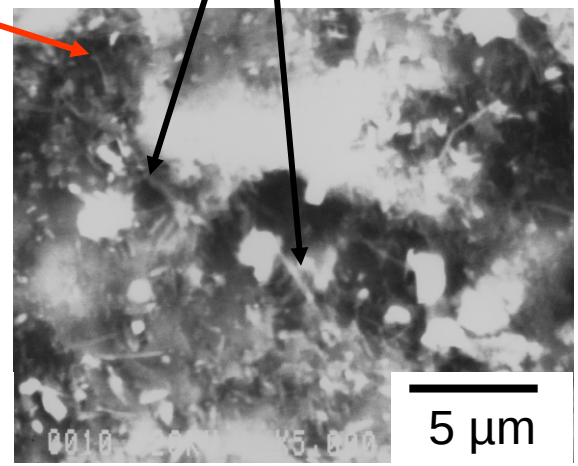


SiC繊維束内部のマトリックス　SiC繊維束外のマトリックス　直径150nm程度のCNF

T-2（CNF添加）

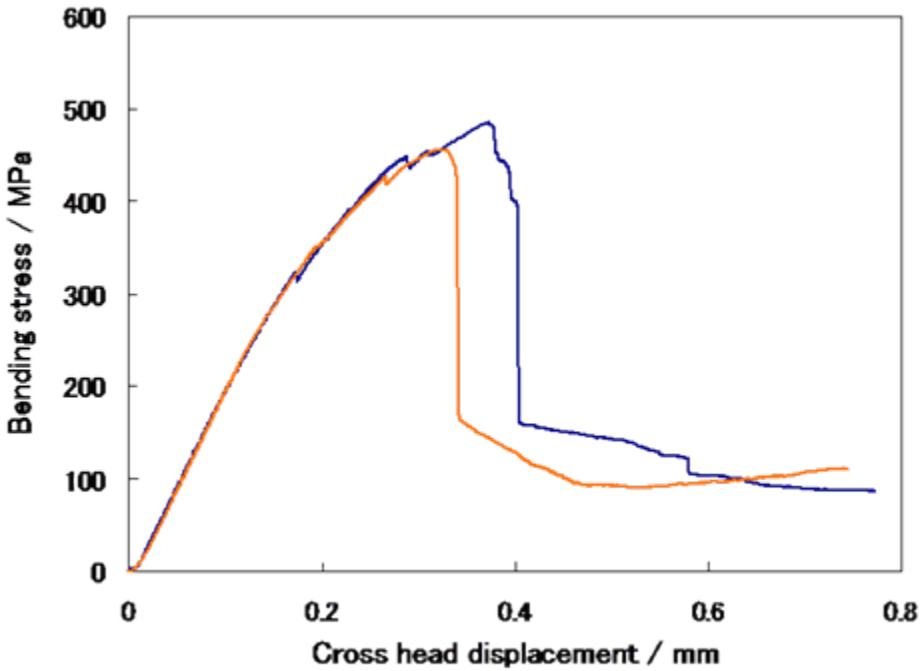




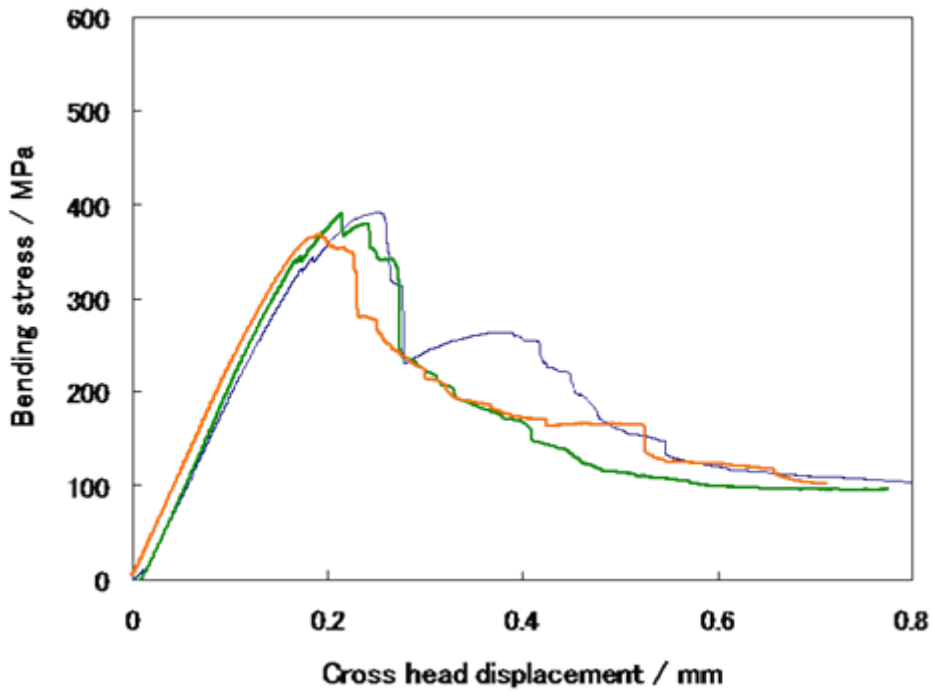


3点曲げ試験結果

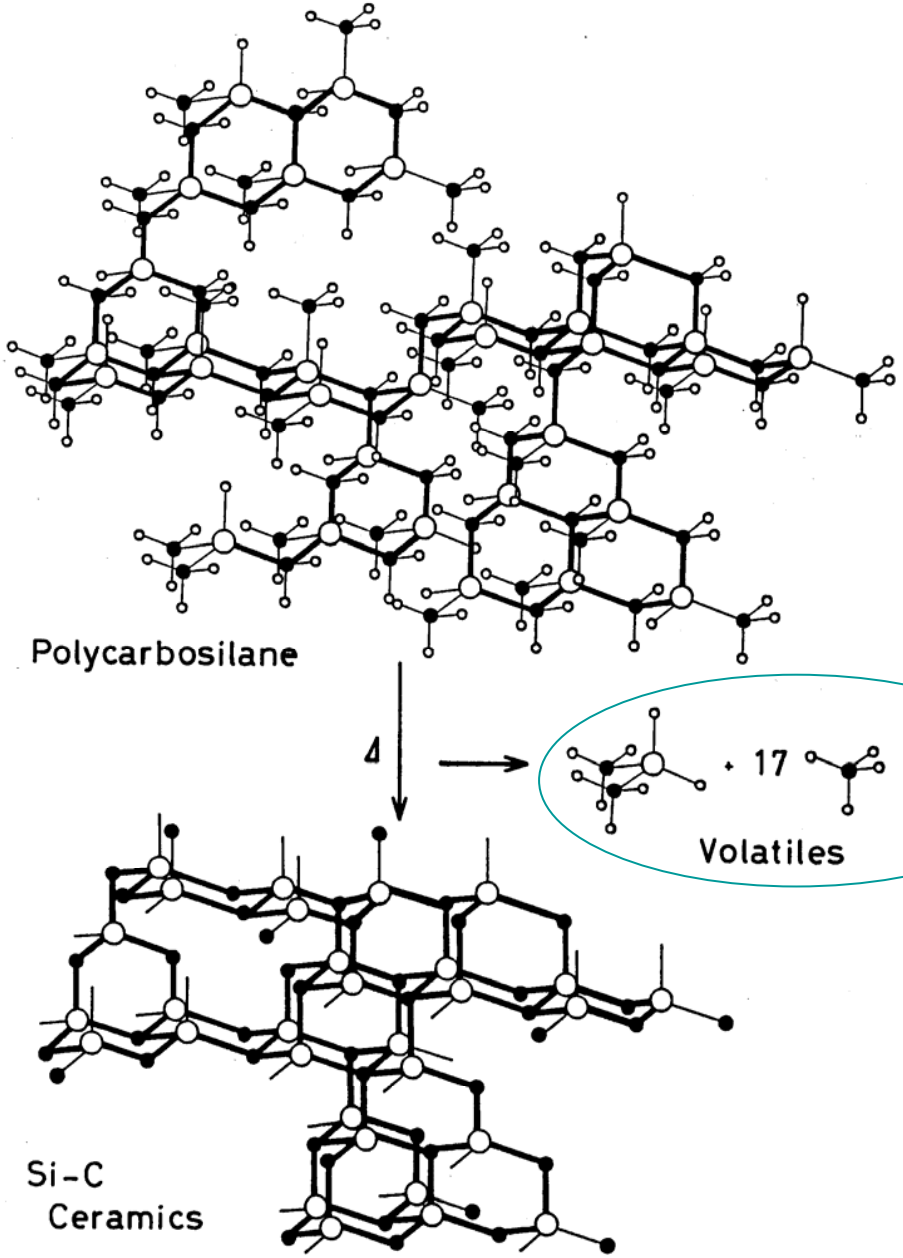
T1（CNF無添加）

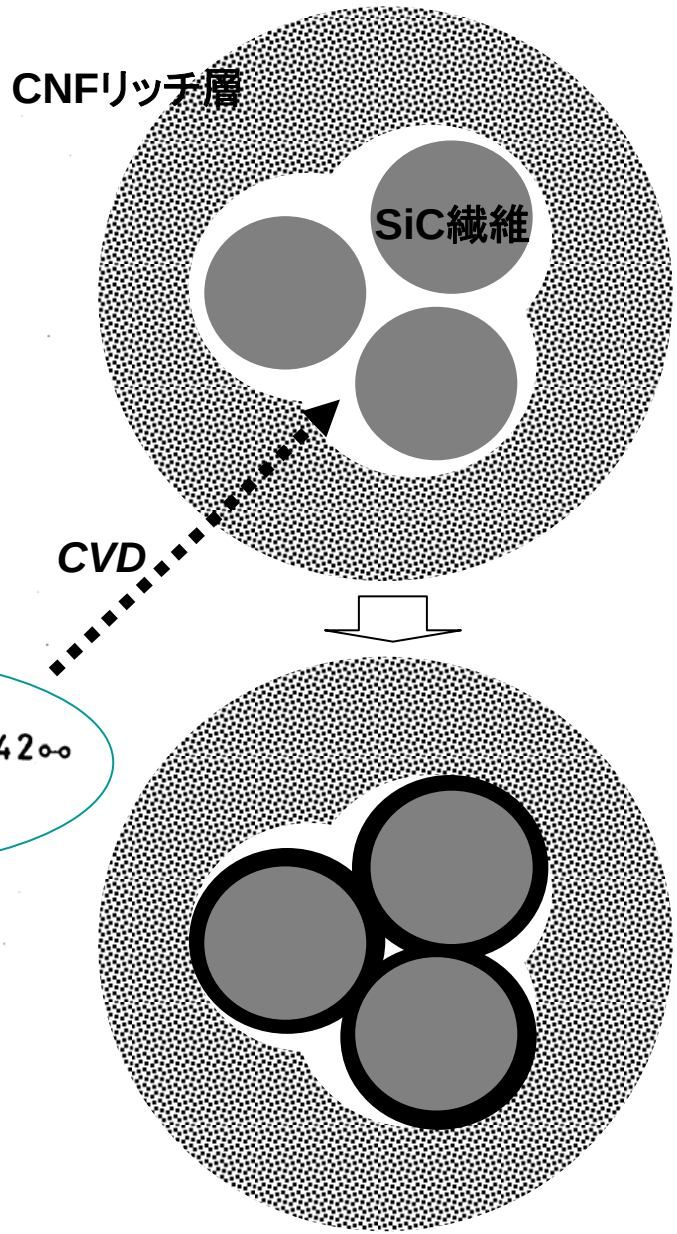


T2（CNF添加）



ポリカルボシランの熱分解プロセスでのインターフェイズの生成

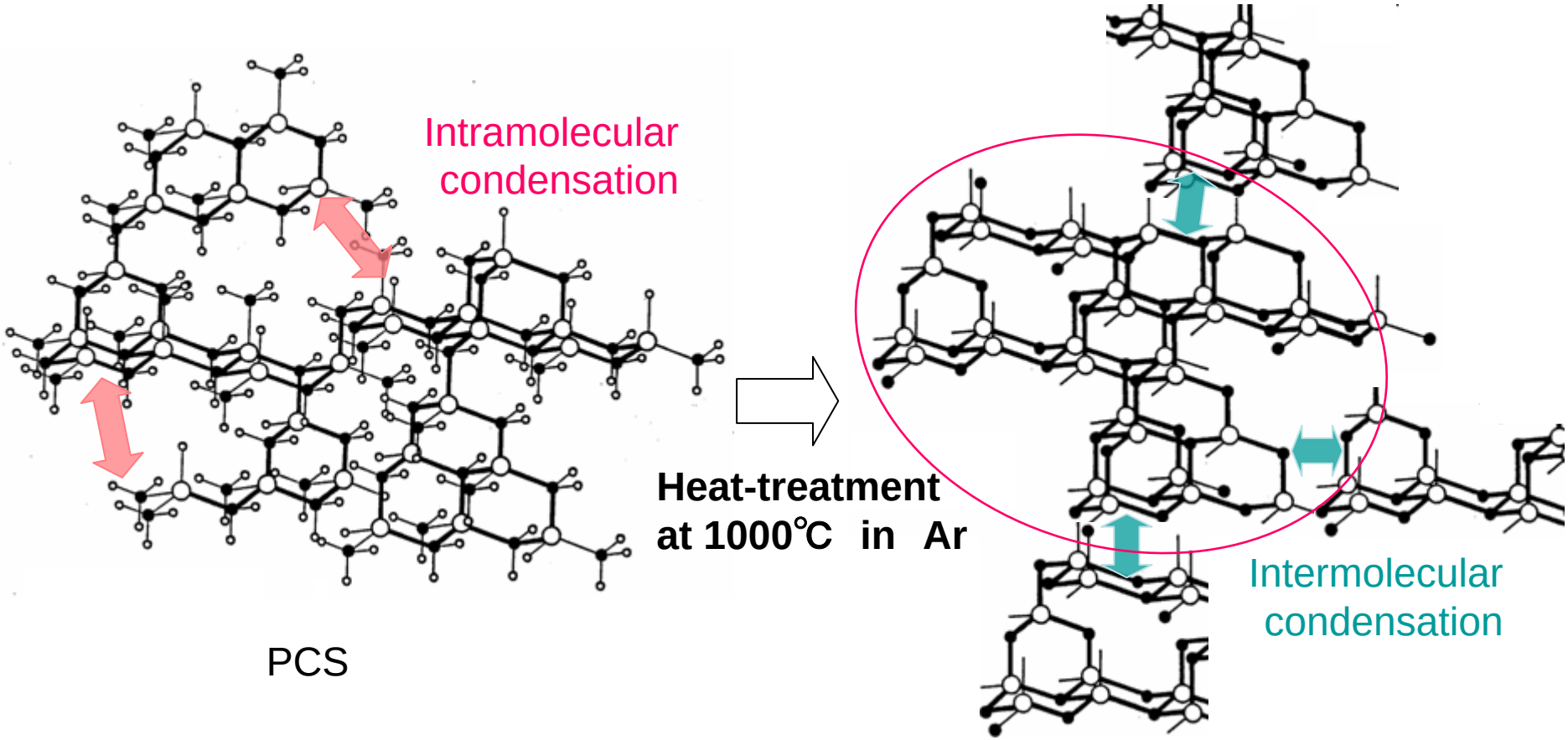




PCS-UUH ナノ粉末をバインダーとするSiC/SiCの作製

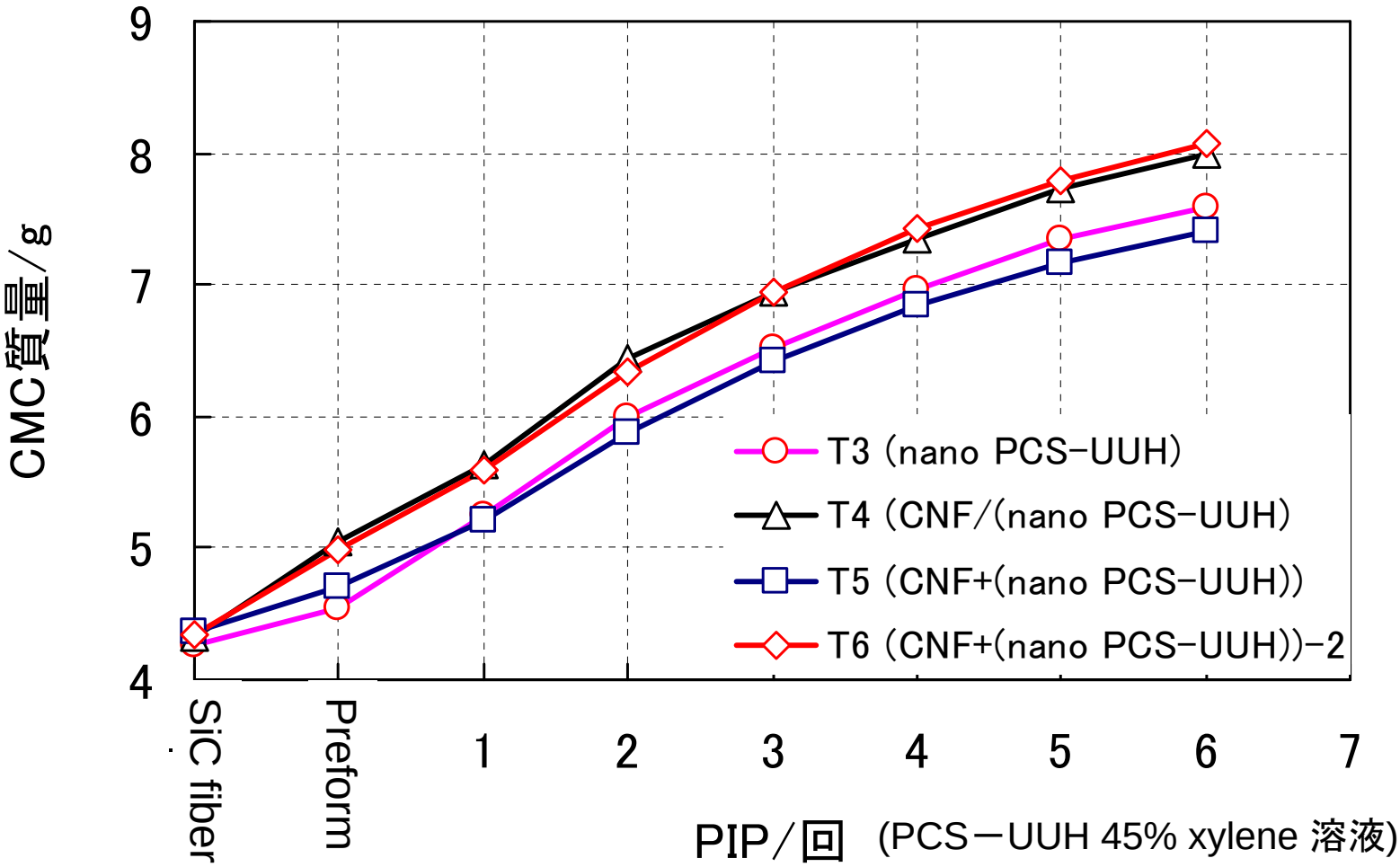
PCS-UUHの溶融状態を経ない自己焼結過程を利用する

PCS-UUHは溶融状態を経ることなく1000℃でセラミック化するが、分子間縮合でSi-Cセラミックスナノ粒子間にネットワークを形成し焼結する。

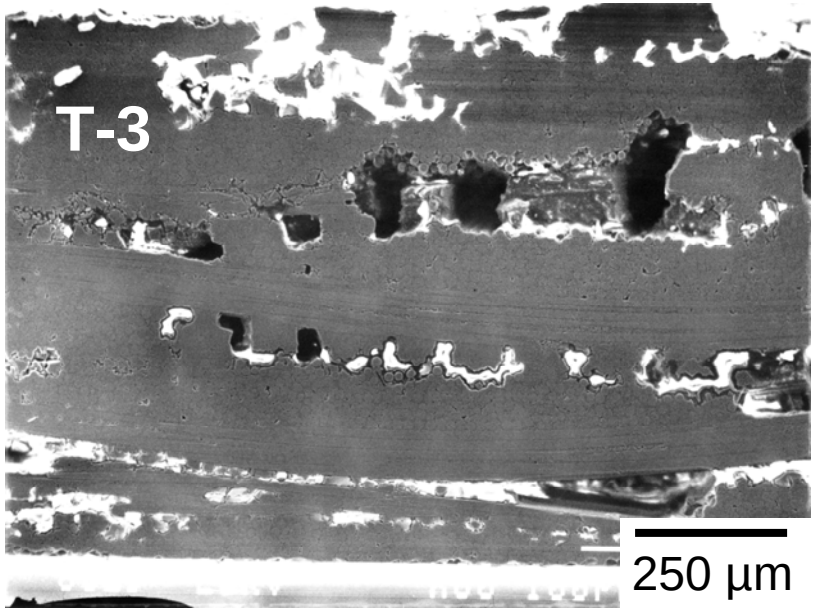


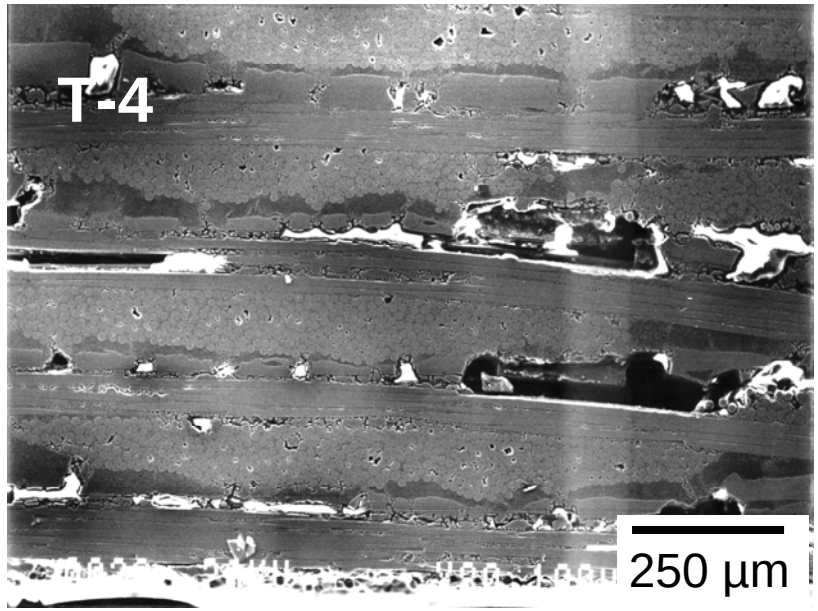
フィラー(PCS-UUHナノ粉末)成形法SiC/SiC複合材料の作製

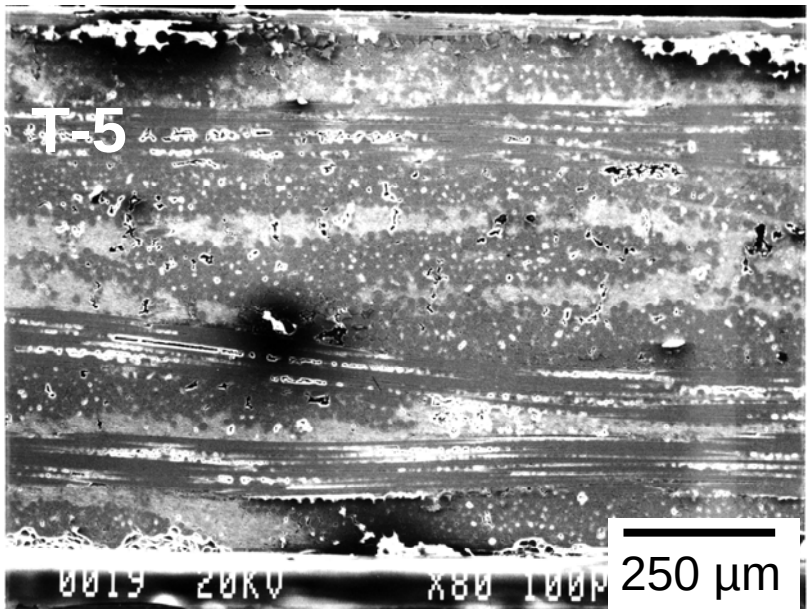
T-3:織布の片面にPCS-UUHナノ粉末を織布の片面に塗布
T-4:織布の片面に**CNFを塗布後PCS-UUHナノ粉末を塗布**
T-5:織布の片面にCNFとPCS-UUHナノ粉末混合物を塗布
T-6:織布の**両面**にCNFとPCS-UUHナノ粉末混合物を塗布

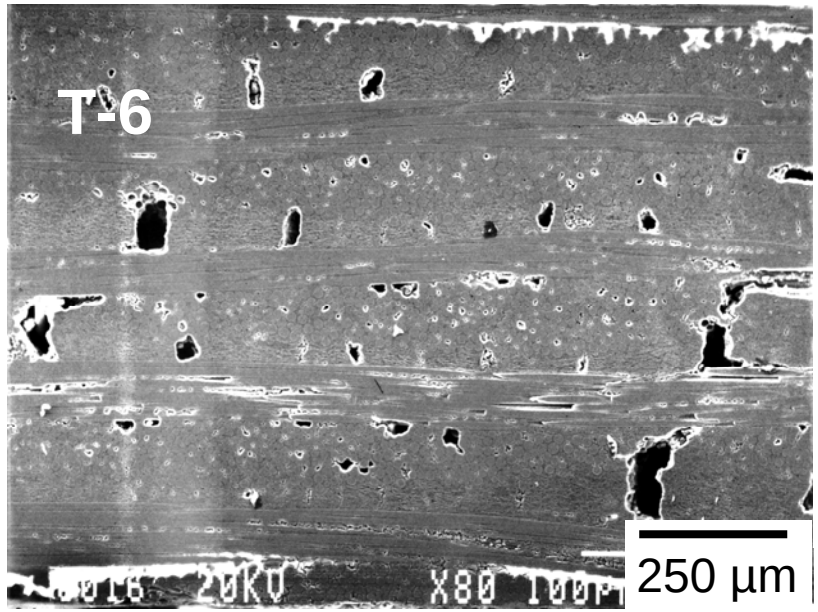


フィラー(PCS-UUHナノ粉末)成形法SiC/SiC複合材料の断面SEM観察結果

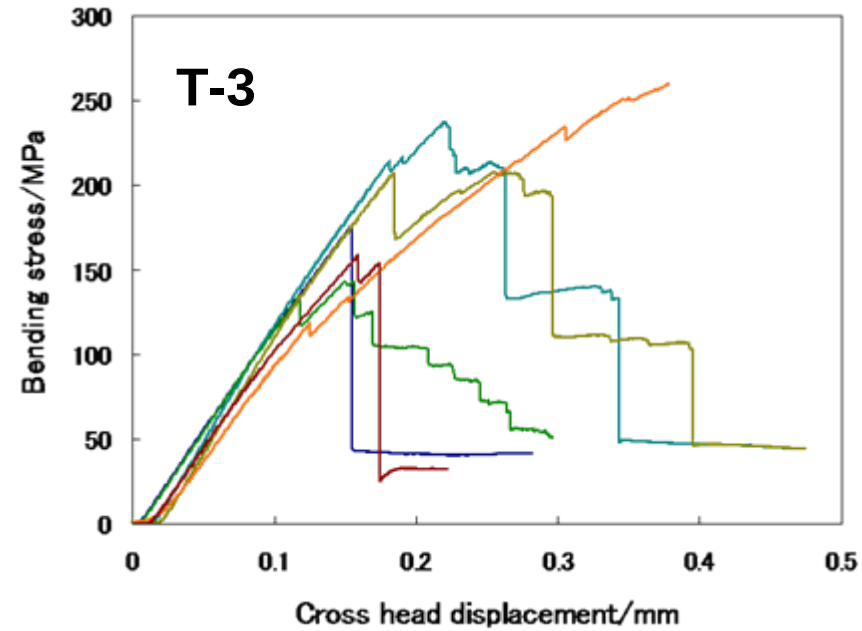


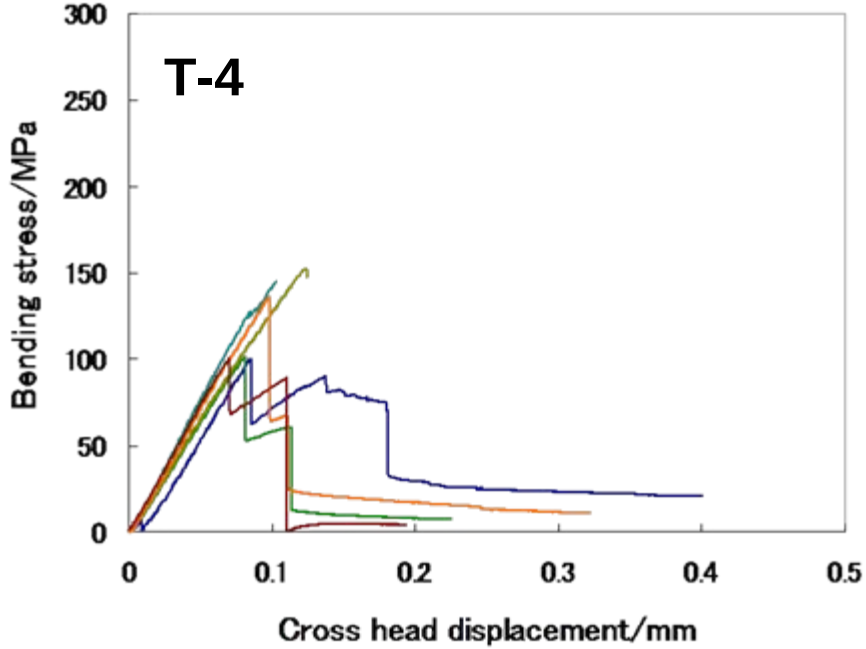


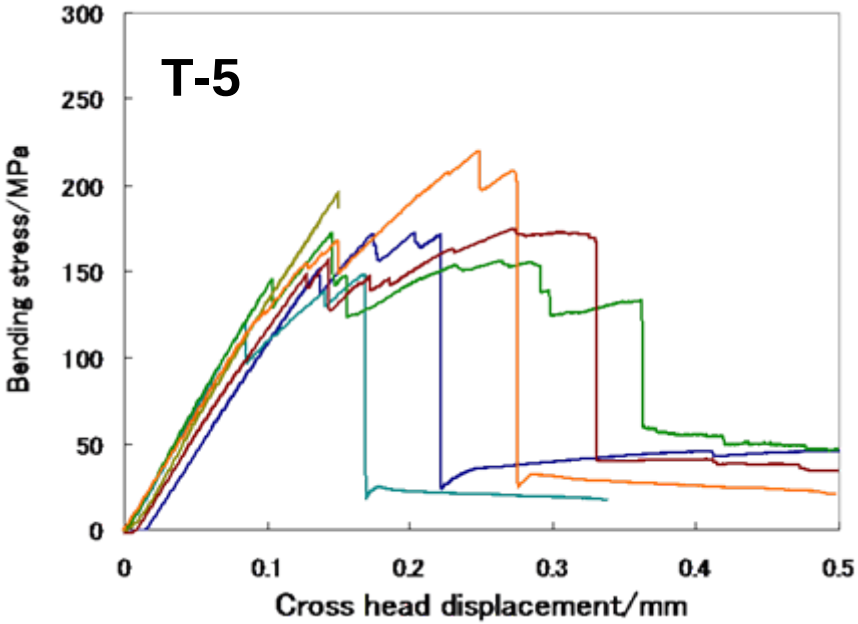


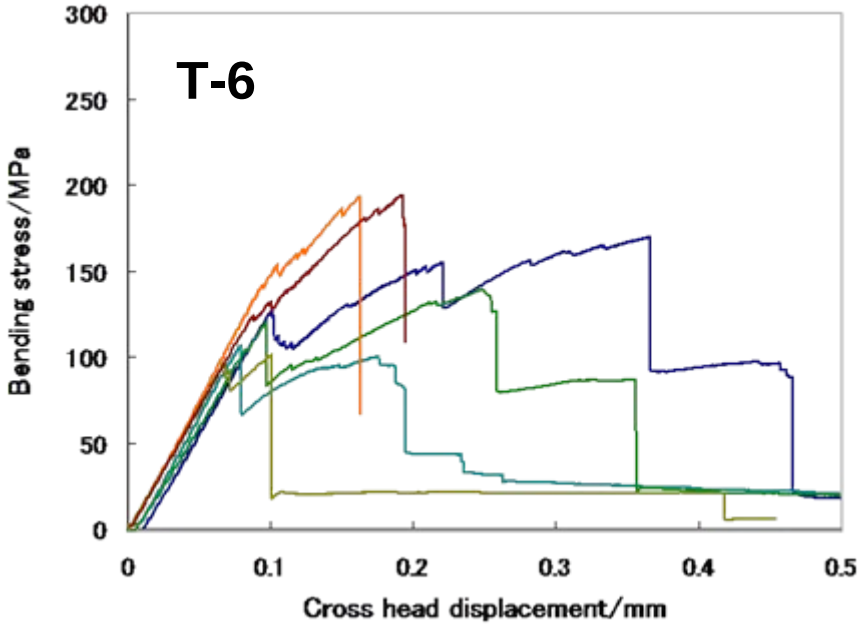


3点曲げ試験結果


T-3
Bending stress/MPa
Cross head displacement/mm
0
50
100
150
200
250
300
0
0.1
0.2
0.3
0.4
0.5

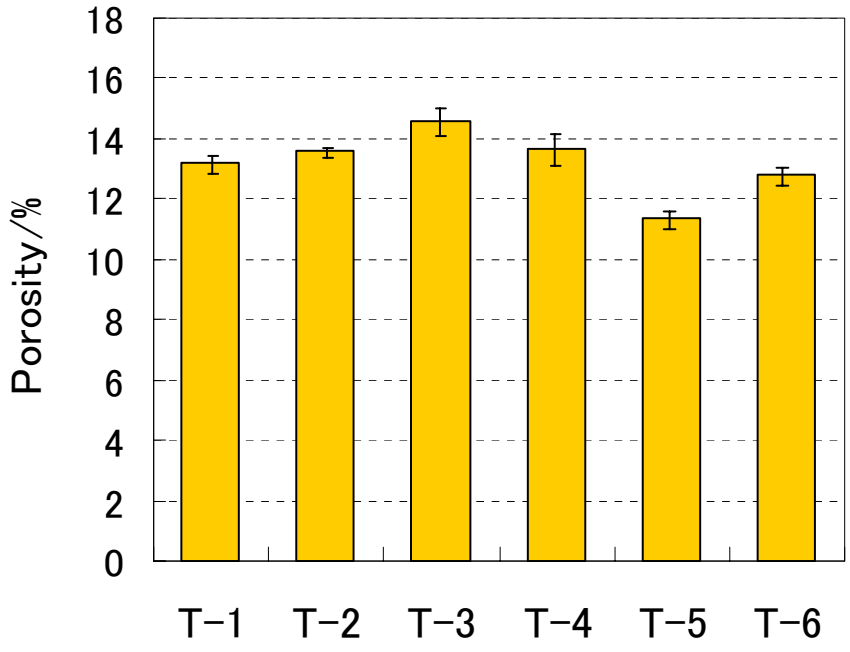

T-4
Bending stress/MPa
Cross head displacement/mm
0
50
100
150
200
250
300
0
0.1
0.2
0.3
0.4
0.5

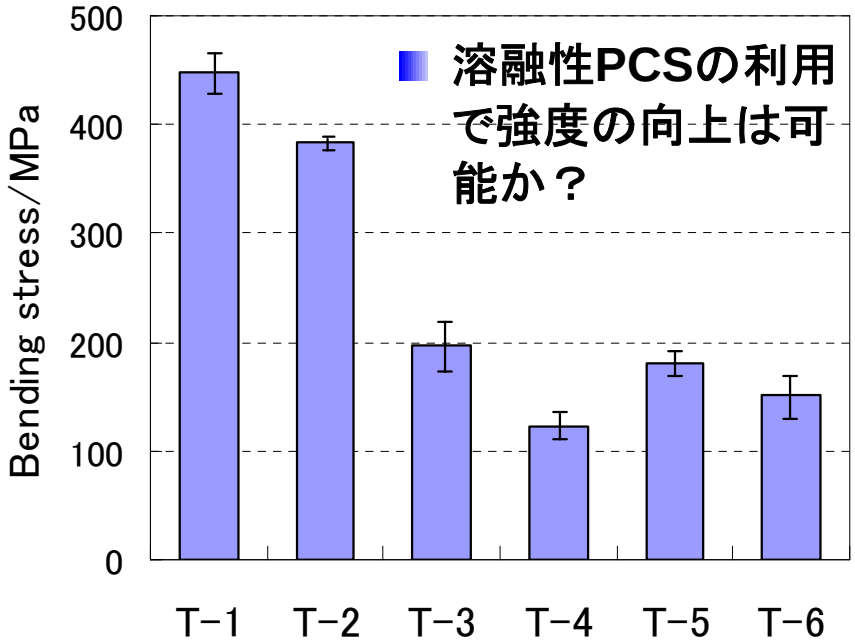

T-5
Bending stress/MPa
Cross head displacement/mm
0
50
100
150
200
250
300
0
0.1
0.2
0.3
0.4
0.5


T-6
Bending stress/MPa
Cross head displacement/mm
0
50
100
150
200
250
300
0
0.1
0.2
0.3
0.4
0.5

まとめ

- APIPで気孔率は従来のPIP法の1/2



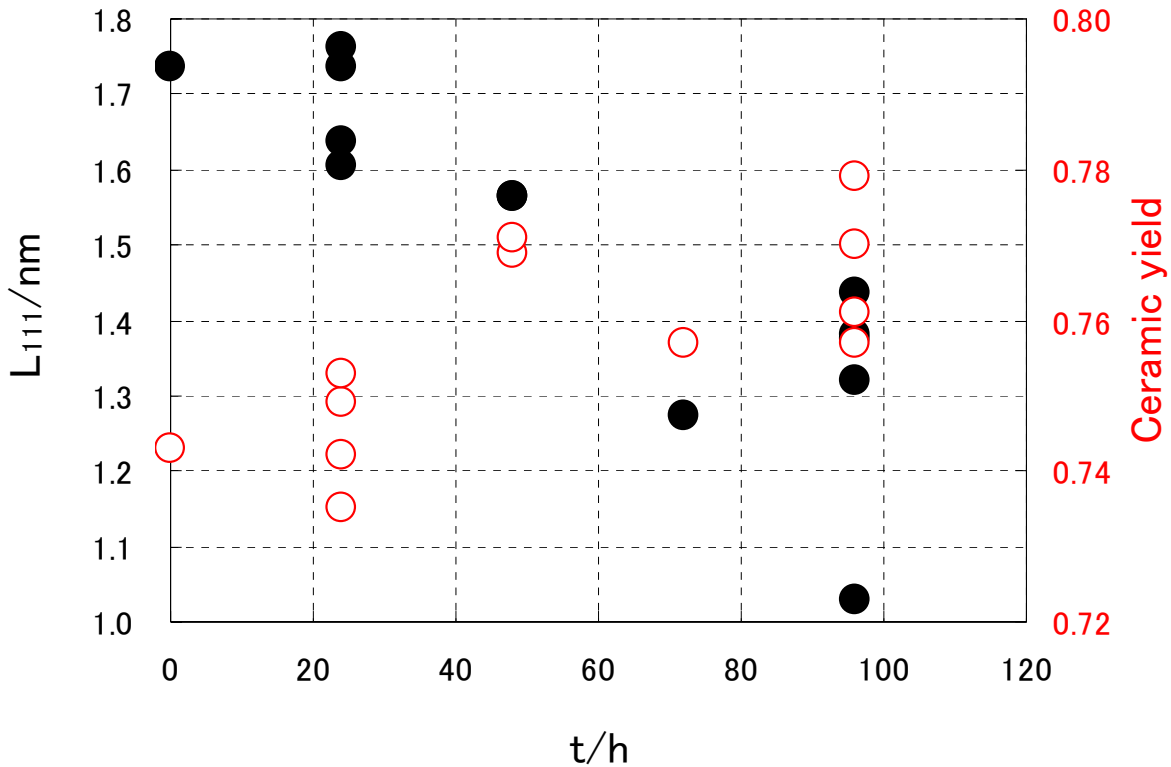


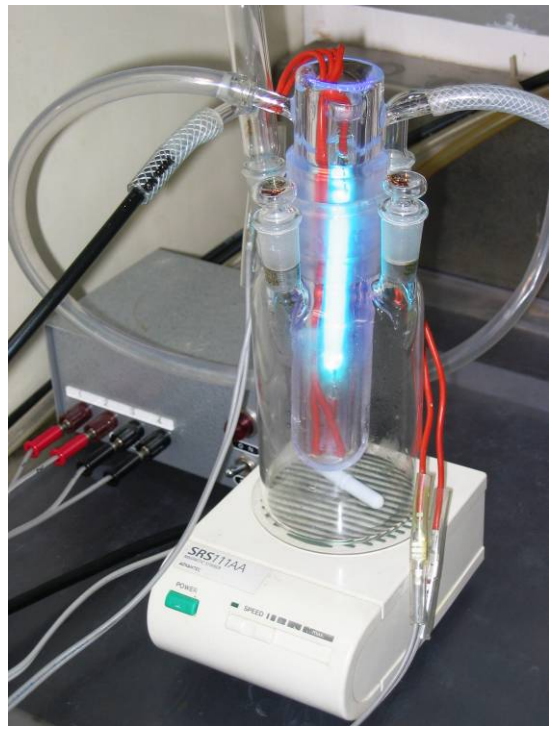
- フィラー成形法によるマクロポアの消滅を実現し緻密化SiC/SiCの実現性を確認
- 不融性PCSナノ粒子の自己焼結を利用したプリフォーム形成に成功
- 不融性PCSナノ粒子の熱分解によるインターフェイズのその場形成を示唆

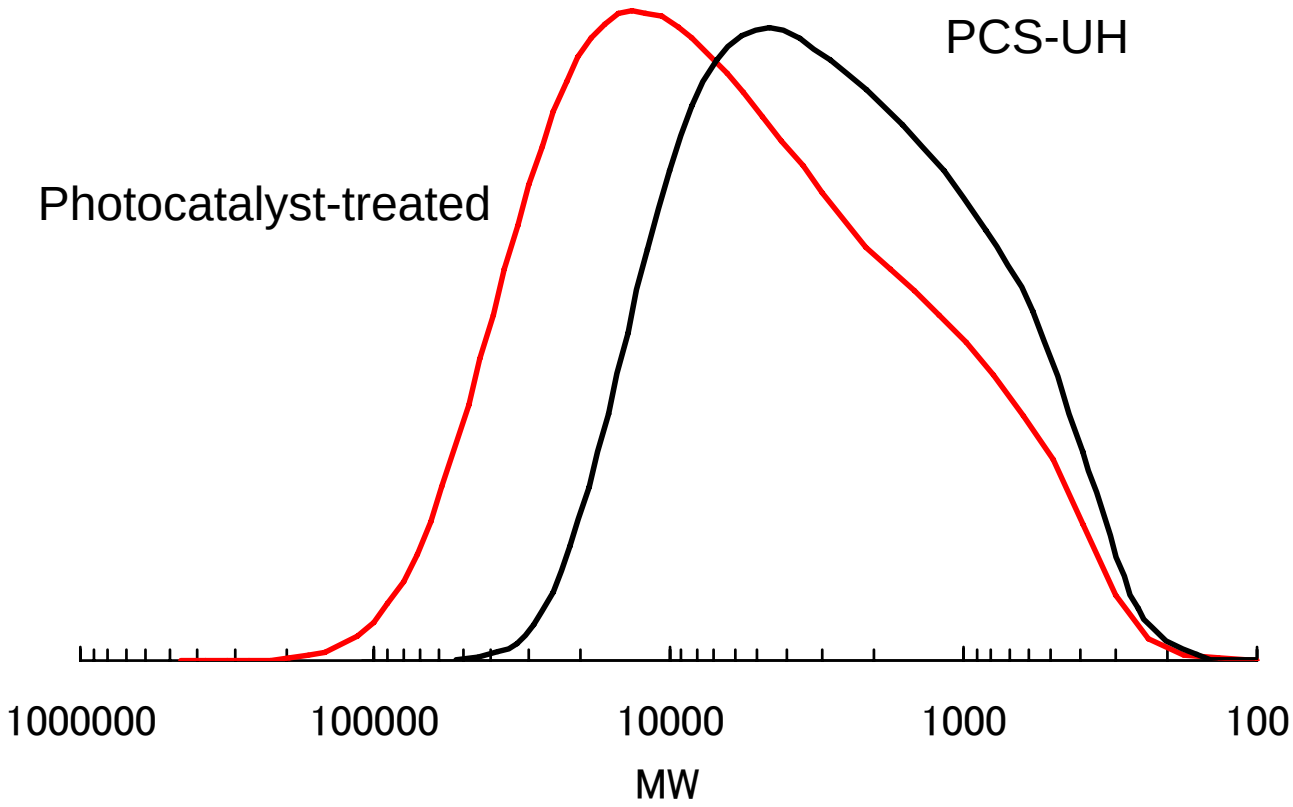
光 (触媒) 反応法

$$\text{PCS/Hexane} + TiO_2\ \text{nanosheet} \xrightarrow[>90\%]{h\nu} \text{高分子量PCS}$$

光触媒処理時間とセラミックス収率、Si-CセラミックスのL$_{111}$



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Photocatalyst-treated
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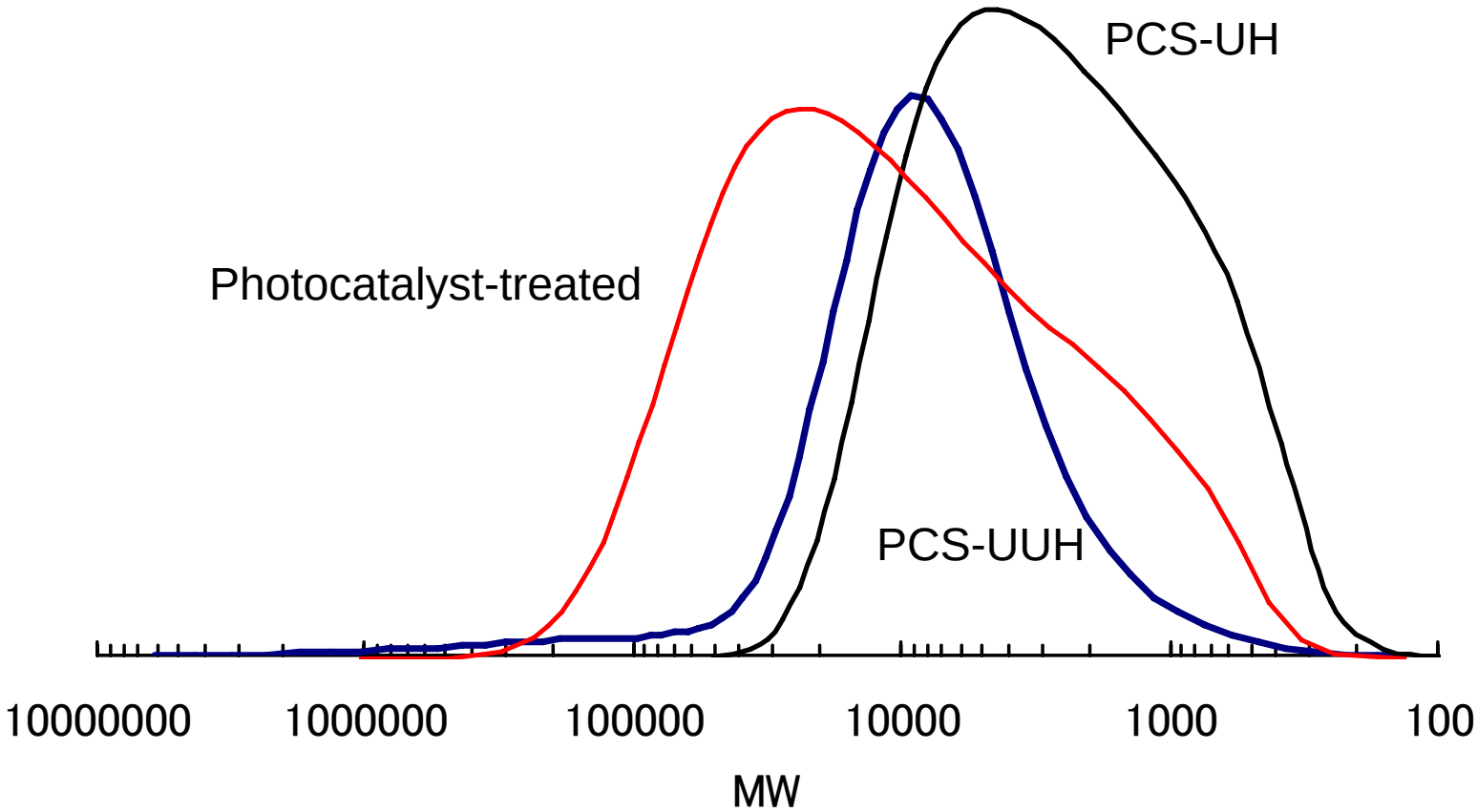
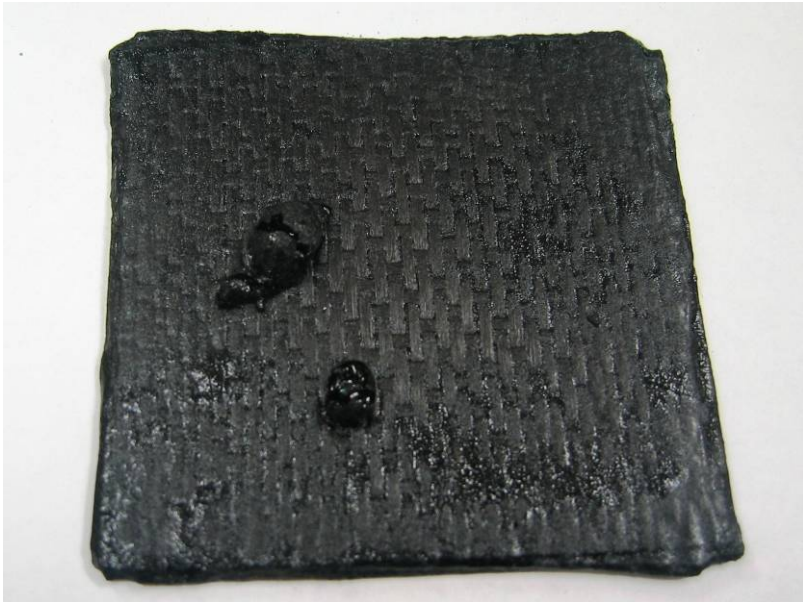
100000
10000
1000
100
MW


PCS-UH
Photocatalyst-treated
PCS-UUH
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1000000
100000
10000
1000
100
MW