

令和元年6月20日現在

機関番号：13601

研究種目：基盤研究(C) (一般)

研究期間：2016～2018

課題番号：16K04947

研究課題名(和文) Si・C溶質が連続供給される溶剤金属からの改良TSSG法によるSiC溶液成長

研究課題名(英文) Solution growth of SiC by improved TSSG technique from metal solvent using SiC ceramics

研究代表者

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交付決定額(研究期間全体)：(直接経費) 3,700,000円

研究成果の概要(和文)：炭化ケイ素(SiC)について、従来の溶液法とは異なり、Siを含まない金属溶液にSiCセラミックスを溶解させ、SiおよびCが溶け出した熔融金属からの結晶成長を行う。熔融金属とSiおよびCの溶解度と溶解速度、4H-SiC結晶成長の安定性、再現性の観点から、この結晶成長に適した金属溶剤および結晶成長条件の最適化を試みた。

溶剤金属としてCrを選択することによりSiCのみを晶出し、溶質であるセラミックスをカーボンるつぽに接しない凹型にすることにより、溶剤中のSiおよびC組成を均一にでき、より厚いSiC結晶を成長できることを見出した。成長条件を改善することにより、より長尺なSiC結晶成長の可能性を示した。

研究成果の学術的意義や社会的意義

従来行われているTSSG法によるSiC溶液成長では、成長が進むにつれて溶液中のSiおよびC組成が変化するため、次第に同一条件下での結晶成長を維持できず、長尺の結晶を得ることができなかった。それに対して、本結晶成長方法において溶剤金属としてCrを選択することによりSiCのみを晶出でき、溶質であるセラミックスをカーボンるつぽに接しない凹型にすることにより、溶剤金属中のSi、C組成をほぼ等量の25mol%程度に一定にできることを示すことができた。これらの成果によりSiCの長尺化の可能性が示唆され、今後の成長条件改善により、同一の結晶成長条件下での高品質で安価なSiC単結晶成長の実現が期待される。

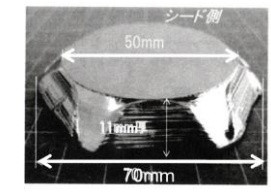
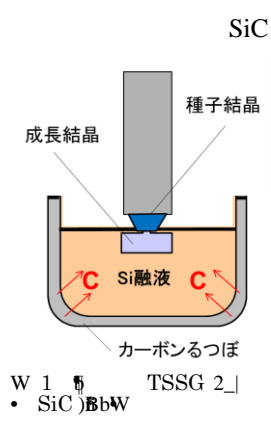
研究成果の概要(英文)：We examined solution growth of SiC from a Cr solvent without molten Si with the use of ceramic SiC feed and a carbon crucible as the SiC solute source. Cr metal was selected for the metal solvent, and we investigated the effects of cylindrical and concave of the ceramic SiC feed. Non-contact between the solution and carbon crucible was realized with the use of a concave ceramic, which maintained the Cr melt within a concavity, whereas the melt contacted with both the carbon crucible and ceramic for the cylindrical ceramic. The growth rate was about 16 times as high as that of the cylindrical ceramic. We found that C and Si concentrations in the residual Cr-based solution were almost the same for the concave ceramic, whereas the C concentration was high and graphite was observed in the solution from cylindrical ceramic. Therefore, we concluded that the use of Cr metal and concaved-shaped ceramic was suitable for the present improved solution growth of SiC.

研究分野：結晶成長

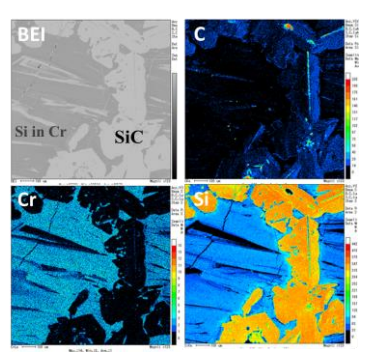
キーワード：炭化ケイ素 溶液成長 改良型TSSG法 セラミック 溶剤金属 溶質連続供給

SiC 3) % b7h 10 Ci 3 b f 9a
 a KZI 8 • IV f s SBI €
 b z d j 6 • Si S 0 A50 f
) (WZ 8 • SiC) B6 x c 2 0 5 % \$
 w 2 I 8 1 1 2 b 2 A 0 8 f E f C 3 Q 3 A b 8 4 6 f
) K Z 2 K Z b A c 1 K S 7 8 Q 9 x
 7 1 K S 7 • 3 a b 4 W 0 G 8 0 W Z
 _ W Z 3) 8 r 1 8 W Z 8 •
 M % Top-Seeded Solution Growth & TSSG 2 W 1 > A €
 SiC b P 6 x 6 M % E 6 5 % f / 8 P 0 9 x
 2 A _) B 0 4 2 > 3) 8 8) @
 6 I 8 • Si _ P c 5 8 / % 0
 b x p _ k x p f (N P 0 K P b Si b 4 8 i
 0 Q K Z SiC) B M G I 8 % \$ 3
 8 8 W 2 8 Kusunoki et al., J. Cryst. Growth
 (2 0 1 3) K K B 6 3 0 P b t (b 3 z 3 8 W Z >
 I j G b 2 b) B 6 0 _ X Z P 0 B 0 8 A
 6) G 0 7 5 8 t X mm b) K ?
 6 G V 8 1 1 M S u _ c 5 b
 P 8 : 8 3 K G 4 (0
 b 3 z 3 8 i e 8 0 i j 1 M •
) B _ 6 K Z Si c 0 i v A C 3 0 9 2 A _ 8 •
 G 0 7 6 K K SiC b P 6 x c Si j 8 i
 B b 0 1 2 8 8 8 M 7 H
 ~ SiC P 6 b % E * . Si) B 6 8 1 0
 8 8 8 f Q b K Z q) B 6 2 8 / % 0 &
 \ P 0 b 4 8 r) 2 A 8 SiC 8 0 B
 6 0 7 s 3 3 K Z 8 •
 G 0 6 K SiC b 8 0 K Z 3 8 0 % , &
 b # T 7 i C 0 SiC) B 6 4 v 1 0 0 % , 7 A
 8 8 8
 TSSG 2 K S Si z B _ u
 r 8 P 0 SiC) B b 8 K S ?
 0 b x p _ SiC b 8 i Q b V _ 5
 ' P c K Z Cr 4 8 / % 0 8 K S Cr _ c SiC
 \ Cr \ Si 0 4 8 s 0 0 8 Cr / % @
 c SiC 8 i b 8 p 4 E 8
 P 0 8 1 G M f 0 p 5 b Si \ C P 0 _ P 0 Z
 M G \ Q b P 0 SiC) B 6 8 4
 8 b) 8 E Z % E b % T • W S Cr
 c Si 8 C (U 2 0 a t % P 0 8 0 6 8
 I 0 6 8 K S SiC 8 i 8 K 1 / 4
 , 8 M K 6 b SiC) b B 6 8 .
 A % E _ 6 M f 0 8 8 W Z 8 •

SiC 6 8 0

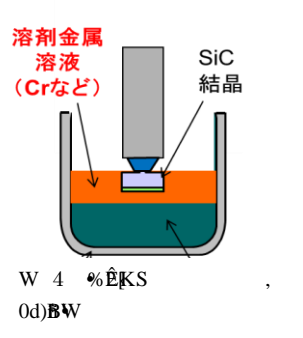


W 2 TSSG 2_B
 1 8 SiC)



W 3 0 8 SiC 8 i
 V 4 8 K S Cr / % 0 b EPMA D
 K SiC 8 B K Z 8 •

SiC 8 5 ' P @
 KS P / % 5 8) SiC 8 i
 8 (b SiC) P c 5 3 8 i _ 8 \
 _ 8 SiC P 6 b 8 h t % K) b 8 k
 i f 3 b % E 8 P / % 5 \ Si 8 C b P 0 8
 0 2 0 4 H - SiC) B 6 b 8 0 (G b)
 B _ 4 : KS 5 ' P c 8) B 6 8 q 4 : 8
 8 0 P M 8 V _ X 8 Z 0 M •



- (1) 1 % 8 8 Cr Ti Ni Fe 8 SiC b P 0 8 0 2 8 0 8 *
- / % I P c 5 & Ni Fe 8 SiC) B b 8 Z
- (2) 2 % 8 8 Cr Ti 8 SiC) B T 0 8 8 8 E 8 b)
- B b 8 8 8 B 6 b 8

(3) 3 % 8 % 2 8k 50mmSiC)B5)B6b2Ab0

1,% Eb%

q Pc5 & Cr Ti Ni Fe B SiC Ń b P000000

TM 0000sb CZ)B(tc)b,AVF00

x 018B_WZc 2000°C

SiC Ń 0 ASiC0 3.14g/cm³b 1600> 2100°C

(>)SiC PB6x83I

@ (>)gW? Si \ C 0p5 P0Z (>)%I 1200> 2000°C

Cr Ti Ni Si 8Z8> SiC Ń V_Pc5 44K

9x05 %0KX6KS<7KT9KS<5 14P

0ZVdK49Sb SiC Ń b55b3Q7eS5 K0

KZ8468e9>h0E0 SiC P0Z88

g/cm²i sec05 Hb3Q7e

r SiC Ń 0P0ZE800

SiC Ń 2Ab8p_8K q [P0Z888I

€Z SiC K p_i/%0KS5 K0M14M0

Qb7• SiC Ń 24E8 P0Z888I Pc5 “ P

0ZC8Kp2A0Kb)B98

s 09K0%I Pc5 & Ni Fe B SiC)B

r 4:KS2Ab8p8e 1 8 SiC Ń g Pc5

€ Ar 7V¼ 1 05 %0M0 q 0bVWS Si> C b P0Z4)

M6S_8H_4KS SiC)B/% 5 /8_K0fO SiC

b)B668W 5 g> H28 079K00%I@ 1500°C

Ni g Fe 5 K)0T0S%6b0V 0QWS)

%Vb (4:K0ZM0)00b

0003)0P/%0000b

28 0%\$ 20mm6k 10mm b SiC)B6M0% M5Mf

3e SiC)B6K868cI)B8 b50e H28

018K H29 0618Qb00Sub989te

t 9x%15 & Cr Ti> SiC)BTD00MeB)B4p8

H28 0 s 0p1*4T00I 1500°C Cr Ti 8S SiC)

B00B6M00KZq4:0 4H b

SiC)BMC8u8o% c8r6K9>B6xTEB U

000CSuT00 K0B60bSu s

_Z/%15 QWS9;KZ/8ZISE_Z18M1#

€c s V 060)000M0

u SiC PB6xES)B6b0

t 0 CZ 2 Si)B6Br_WZ85)B6bSub8

€0b (4:10E00M)9%0b+ SiC PB6x

4:K3) SiC PB66x8Z0M0

v %\$ 2 8k 50mmSiC)B2Ab0

t u 0 2 8 K s t]

_ SiC PB6(0)00c s t 003)(x

0X8Zc0 X)z00M0rS)pb500

(00) TOF-SIMS (000M040000e

1_0 30 0%\$ 2 8k 50mm b 4H bM0x

3)0 100cm⁻²b SiC)B% M0

2,% EbY

(1) B 28 0 b8oBÝ

00B/0ZK Pc5 & Cr Ni Fe B SiC b P00

P0Z00 0e SiC Ń Kpb P0ZE000)Pc5 “

& Cr Ni Fe B SiC)B0KS

rN Pc5 † Fe KSc0 SiC Ń 000Kpb P0Z

000VSi SiC Ń 0)VKS Fe ?

€ SiC 00%0b PcKZc4:5r)1=KS

_ Pc5 † Ni KSc0 SiC Ń b P0Z0AS0I

KS Ni 0 SiC)B0 Ni-Si 00W

Z Ni v PcKZc4:58KS

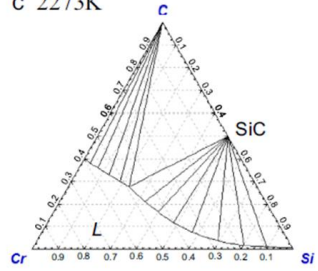
Pc5 KZ Cr 8Sc0 Ń V_KS Cr ? SiC)0A

SrS SiC)%W_ SiC)B6M0v050FGI SiC

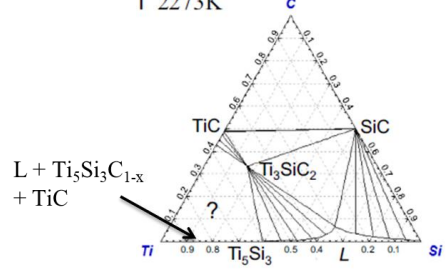
b)B6300000SQ0 Cr 7Pc5 KZ80

Cr-C-Si三元系状態図
 Ti-C-Si三元系状態図
 Mn-C-Si三元系状態図
 Ni-C-Si三元系状態図

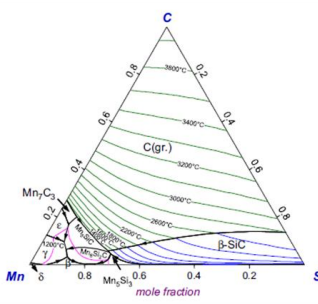
a) Cr-C-Si三元系状態図
 c 2273K



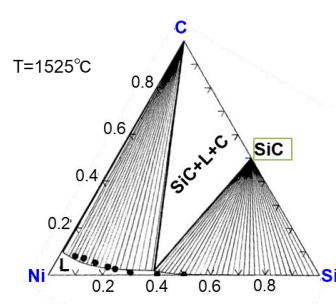
b) Ti-C-Si三元系状態図
 f 2273K



c) Mn-C-Si三元系状態図



d) Ni-C-Si三元系状態図



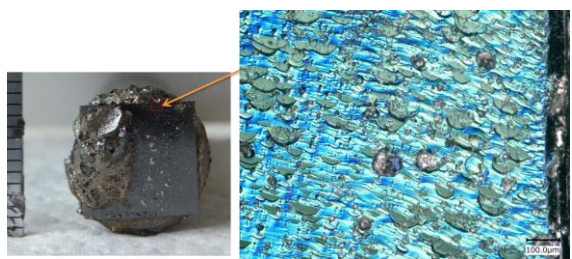
a, b) T. Narumi et al., J. Cryst. Growth 408 (2014) 25–31.
 c) M.-K. Paek et al., CALPHAD 46 (2014) 92–102.

d) Y. Du et al., Metall. Mat. Trans. A 30 (1999) 2409-2418. の図の向きを変更

W 5 Si> C> M& M: 5 “ Cr, Ti, Mn, Ni(U) (W)

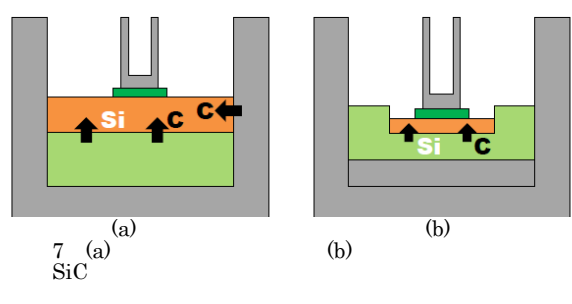
(2) B 29 Ø b8oBÝ
 Pc5 KZ c B 28 Ø 4: f8KS
 KSW 4 b(W_8Z)B6×
 5-15mm PÖÄ 3-21¥ /cm b(VIO Z)
 W 6(a)b(8B6)X8Z/80Ø

Cr Py@
 W 6(b)cB6KS)/8b8g
 6Mf6f
 B6KZ4C Py5 “
 bÜTb fEg?
 B6x/83 fWZ8S
)_v3r fKS) f.
 P@ 9I8B63Ø
 98c) iKcC 4H B6K@
 4H B
 SiC)B6MG(V8S
 4H M
 B6KS B63W S
 Cr Pc5 KZQKS)B ÖÄ
 Al 4EKScæ SiC f
 VKS Al f SiC)c f b
 Al c Pc5 KZM(6)l= fS
 Al4C3



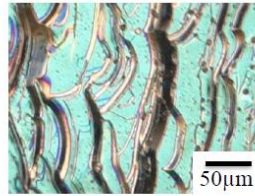
(a) Cr
 (a) Cr
 (b) (b)

(3) B 30 Ø8oBÝ
 B 29 Ø PyKZ4:G@
 6G@S9x%15 f
 6• Cr PKZ P2A*
 f b g f 59\
 Al MG B68b1
 B63ØZ*8j_X
 8ZØKS
 W 7_&M;_ SiC f

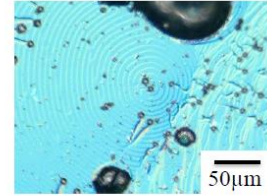


7 (a) SiC
 (a) (b)

7(a) > KOK8
 °W 7(b) > b 2 8@X8Z9KS
 QbY W 8 _GM_ E
 mZ
 @B6KB68c0B6x
] 5GKKS B6x
 EPMA_Kp4gWS5 pb
)B(WSG
 Xp 4#e(NE P0Z]
 -PypbB A2s
 GM G
 Z8GWS EPMA [KS
 M
 SiC_4t4G0AS
 M%o Al MG\B68b
 QMGZMGWS
 Al-C BIE SiC bB6GK
 B6KS
 v/bG
 92Ai Si 85 Py_ SiC PB6 Al e-
 KPC5 pb A0KS TSSG 2c\$ SiC q
 B666f Si C)Bop5b 25mol% M_AGK6
 STK6% KZ8S SiC)b8KS
 b18WS %\$ 2 0



成長速度: 9μm/h



成長速度: 155μm/h

8 (a) (b)
 Si C)B
 Si C Cr bU
 SiC bB6x4:K
 5 (b 1 b 0.1# m &
 Al † 20mol KS Py
 10mol% b Py

3 z=e 1/4
 6 b

- 1) K. Suzuki, T. Taishi, Solution growth of SiC without molten Si using concave ceramic SiC feed, The Proceedings of the 8th Forum on Science and Technology of Silicon Material 2018, pp. 377-381, 2018.
- 2) N. Tsuchimoto, S. Ehara, T. Taishi, Numerical simulation of carbon concentration in top-seeded solution growth of SiC, The Proceedings of the 8th Forum on Science and Technology of Silicon Material 2018, pp. 377-381, 2018.
- 3) K. Suzuki, K. Hyun, T. Taishi, Effect of the Growth Conditions on the Crystal Quality in Solution Growth of SiC Using Cr Solvent without Molten Si, Material Science Forum, 924 (2018) 35-38.
- 4) K. Hyun, T. Taishi, K. Suzuki, K. Teshima, Experimental Determination of Carbon Solubility in $Si_{0.56}Cr_{0.4}M_{0.04}$ (M = Transition Metal) Solvents for Solution Growth of SiC, Material Science Forum, 924 (2018) 43-46.
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- 6) K. Suzuki, T. Taishi, The Solution Growth of SiC from Solvents With or Without Si, Proc. of The 7th International Symposium on Advanced Science and Technology of Silicon Materials, pp. 297-300, 2016.

20 b

- 1) $\hat{D}N$, 5eE, u%\$(, SiC PB6xP2Ab P0Zz3B6x, 2019, 164 Gln, 3/4, 2019, 3 v.
- 2) u%\$(, NÄ, $\hat{D}N$, SiC P0 Et(0)NS0, 47 G)B6Y, 2018, 11 v.
- 3) 5eE, $\hat{D}N$, P2Aj) % bggIOS, Cr M Pyb, SiC PB6x, 47 G)B6Y, 2018, 11 v.
- 4) $\hat{D}N$, SiC PB6xP0bt(0)B6b80Z, 102 G%É, 2018, 3 v.
- 5) $\hat{D}N$, SiC gBB, 65 Gln, 2018, 1 v.
- 6) $\hat{D}N$, TSSG 2, SiC PB6xPypbt(0 P0Zz30Z2A, 12 G6%É, 2017, 12 v.
- 7) $\hat{D}N$, 1/4, Si_Cr_C g, Si_Cr_M_C (M=Co, Mn) Py, SiC PB6x, 12 G6%É, 2017, 12 v.
- 8) 5eE, 9%, u%\$(, $\hat{D}N$, N, N-, SiC PB

- 4 4 G1n ‡ , XCd , 2017 ° 11 v .
- 9) 9* , 5eE , C9× , ĐN , SiC P0E8 , 7 3 0 3 5
 - 10) N. Tsuchimoto, K. Suzuki, M. Takahashi, K. Hyun, T. Taishi, K. Murayama, S. Harada and T. Ujihara, The effect of the structure of seed attachment on polytype and morphology in solution growth of SiC by TSSG method, International Conference on Materials and Systems for Sustainability 2017, Nagoya, Sep. 2017.
 - 11) K. Suzuki, M. Takahashi, N. Tsuchimoto, K. Hyun, T. Taishi, K. Murayama, S. Harada T. Ujihara, Evaluation of Polytype of SiC Grown by Top-Seeded Solution Growth Technique Using Various Composition of Cr in Si-Cr Based Solvents, International Conference on Materials and Systems for Sustainability 2017, Nagoya, Sep. 2017.
 - 12) ĐN , 9* , u%\$(, 5eE , TSSG 2_† SiC P06×E8 , 7 8 G 2 0 1 7 ° 9 v .
 - 13) T. Taishi, M. Takahashi, N. Tsuchimoto, K. Suzuki, K. Hyun, Solution growth of SiC from the crucible bottom with dipping under unsaturation state of carbon in solvent, International Conference on Silicon Carbide and Related Materials 2017, Washington D.C., USA, Sep. 2017.
 - 14) K. Suzuki, K. Hyun, T. Taishi, The effect of the structure of seed attachment on polytype and morphology in solution growth of SiC by TSSG method, International Conference on Silicon Carbide and Related Materials 2017, Washington D.C., USA, Sep. 2017.
 - 15) K. Hyun, T. Taishi, K. Teshima, Experimental Determination of Carbon Solubility in Si_{0.56}Cr_{0.4}M_{0.04} (M=Transition Metals) Solvents for the Solution Growth of SiC, International Conference on Silicon Carbide and Related Materials 2017, Washington D.C., USA, Sep. 2017.
 - 16) 5eE , ĐN , Cr M Py_† SiC P06×E8 0 2 Ab6E , 6 4 G 2 0 1 7 ° 0 3 v .
 - 17) K. Suzuki, T. Taishi, The Solution Growth of SiC from Solvents With or Without Si, 7th International Symposium on Advanced Science and Technology of Silicon Materials, Hawaii, USA, Nov. 2016.
 - 18) 9* , 5eE , ĐN , SiC P062 E 8 0 2 Ab6E , 3 0 1 , 3 G 4 2 0 1 6 ° 1 1 v .
 - 19) 5eE , ĐN , Cr Py_† SiC P06×E8 0 2 Ab6E , 8 0 1 , 3 G 4 2 0 1 6 ° 1 1 v .
 - 20) K. Suzuki, T. Taishi, Solution growth of SiC from metal solvent, 18th International conference on Crystal Growth and Epitaxy, Nagoya, Aug. 2016.

EE

o 1 b

SiC)b04%
 ĐN 5eE%\$(
 E
 IOÁ
 I8^a 2018-038847
 2018 °
 AE

4> %E)E

(1)%E*.
K

(2)%EŠ.
%EŠ. 5eE E
Suzuki Koki

%EŠ. u• E
Tsuchimoto Naomichi

%EŠ. P ≤
Hyun Koangyong