The effect of current on insulating ceramic materials during SPS

2018. 03. 19.

Ryu Jonghun

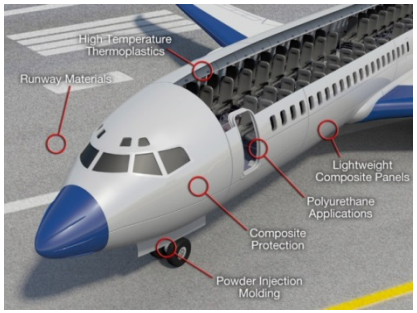
Contents

PART 1.

EFFECT OF ELECTRIC CURRENT ON THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HARD-TO-SINTER MATERIALS WITH HIGH MELTING POINT

Background

- The needs for structural ceramics
  - ✓Devices or parts for severe environment such as high T / strong mechanical load
  - ✓Materials with good properties especially mechanical properties
  - ✓Applications: bearing, automotive, aerospace, robot and etc.



aerospace.basf.com/

Typical structural ceramics

Materia		Advantages	Applications
Oxide	SiO2	Low cost, Easy to process	Tube, Boat
	Al2O3	High T/Wear/Corrosion resistance	Focus Ring
Non oxide	SiC	High T/Wear/Corrosion resistance Thermal shock resistance	Automotive engine parts, bearing
	AlN	High thermal conductivity	Heater Susceptor
	Si3N4	Good wear-resistance at high T Thermal shock resistance	Wear-resistance material

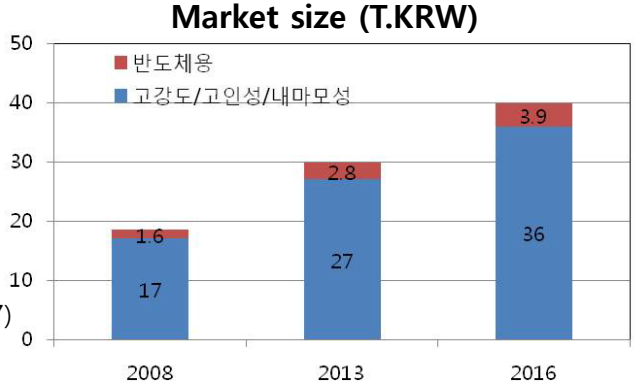
국내외 구조세라믹산업 현황 및 기술동향, (2010)

Background

➢ Domestic market of structural ceramics

구분	2007	2008	2009	2010	2011	2012	2013	2014	2015
수요	14,830	16,771	18,969	21,457	24,207	27,315	30,829	34,804	39,301
생산	10,946	12,260	13,731	15,379	17,154	19,133	21,341	23,804	26,552
수출	3,721	4,212	4,768	5,398	6,110	6,917	7,830	8,864	10,035
수입	7,605	8,723	10,006	11,476	13,163	15,099	17,318	19,864	22,784

세라믹신소재산업 기반조사 (2007)



*출처: 신산업총연 특별기획보고서 (2006, 일본)
Ceramic industry (2005)

✓Sustained growth, but raw materials/materials all imported

✓Technical competitiveness↓ (US, Japan)

-> Develop competitive process technique of structural ceramics

Leading research institutes

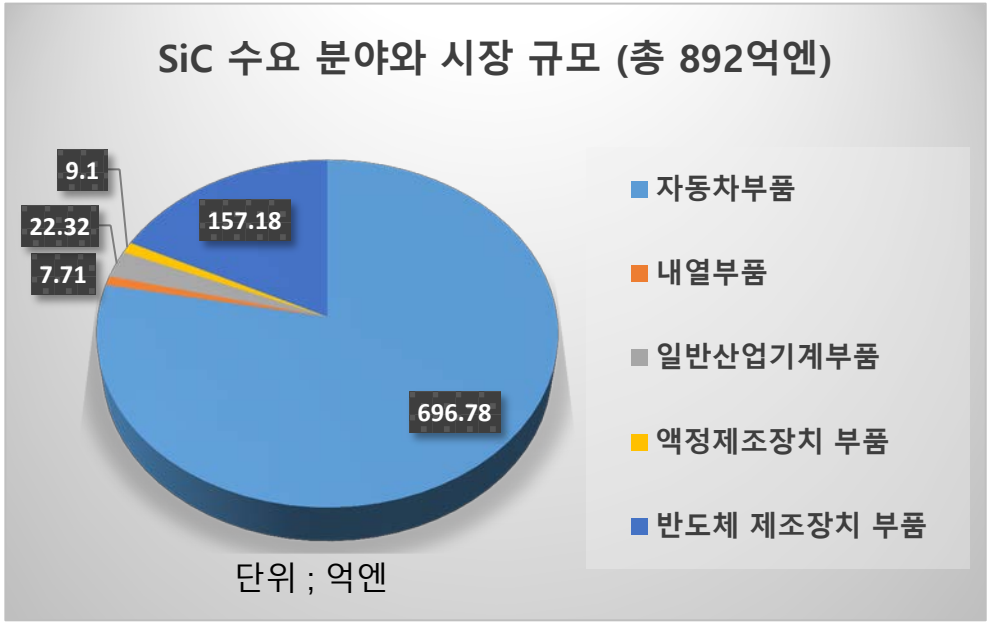
기관명	주요 내용
한국세라믹기술원	• 고열전도도, 고저항 질화알루미늄 소결기술 개발 * http://www.kicet.re.kr
KIST	• 초고순도 탄화규소 원료개발 • 초고순도 반응소결 탄화규소 소결기술 개발 * http://www.kist.re.kr
재료연구소	• 반응소결 질화규소 소결기술 개발 • 탄화규소의 저온 소결기술 개발 * http://www.kims.re.kr
KAIST	• 세라믹 소결의 치밀화 이론 분석 • 세라믹 소결의 비정상 입자성장 * http://www.kaist.ac.kr
SKC 솔믹스, 이노세라	• 대형 반응소결 탄화규소체 개발 * http://www.solmics.co.kr, www.inocera.co.kr
삼성전기	• 나노 $BaTiO_3$를 이용한 극소형 고용량 MLCC 소결기술 개발 * http://www.samsungsem.co.kr

기관명	주요 내용
AIST	• 고열전도도 반응소결 질화규소 소결기술 개발 * http://unit.aist.go.jp/amri/
Yokohama National Univ.	• 질화규소계 세라믹스의 소결 및 역학특성 연구 • 질화규소 볼 베어링 소재의 내구성 연구 * http://www.ynu.ac.jp
Kyocera	• 비산화물계 대형 소결품 개발 * http://global.kyocera.com/prdct/fc/
Sumitomo	• 스프크 플라즈마 소결법의 개발 및 관련장비 개발 * http://www.shi.co.jp/sps/
Covalent Materials	• 대형 반응소결 탄화규소체 개발 * http://www.covalent.co.jp
NGK	• 질화알루미늄계 고열전도 세라믹 소재 개발 • 다공성 DPF 소재 개발 * http://www.ngk.co.jp
기관명	주요 내용
Oak-ridge National Lab.	• 질화규소 계면의 원자구조 및 기계적 물성 • 질화규소 터빈 블레이드의 실장시험 * http://www.ornl.gov/
Ceradyne	• 비산화물계 방탄판의 개발 • 고온가압소결법의 연속공정개발 * http://www.ceradyne.com/
NASA	• ZrB_2계 초고온 세라믹스 개발 • 고온 세라믹 복합체 연구 * http://www.nasa.gov/centers/glenn/

소재기술백서, (2011)

Material selection

- Silicon carbide (SiC)
  - ✓Market conditions and application



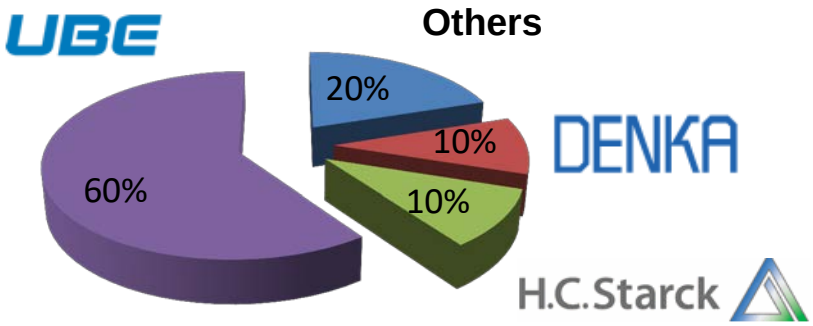
SiC 소결체 및 분말에 관한 조사 (2013)

-> Widely used from high-strength to high-temperature semiconductor materials

Material selection

- Silicon nitride (Si_3N_4)
  - ✓Market conditions

Worldwide market of silicon nitride



Import trend of silicon nitride

MT ; Metric ton

	Japan	Germany	Others	Total
2010	16 MT	5 MT	4 MT	25 MT
2011	16 MT	10 MT	4 MT	30 MT

수출입무역통계 (shippersgate.kita.net)

- ✓ Production volume of major companies
  - UBE (Japan) : 600 MT/year , Denka (Japan) : 100 MT/year
  - H.C Starck (Germany) : 100 MT/year
  - Others : Accumet Materials, Alzchem (US), EnoMaterial (China)

-> No domestic production company !!

Material selection

- Silicon nitride (Si_3N_4)
  - ✓Applications

Structural ceramics

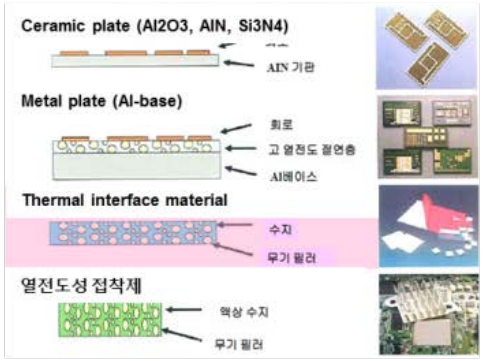
● Engine part

● Wear resistant

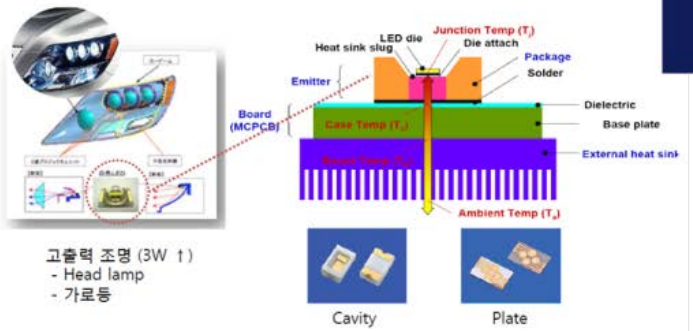
● Aerospace

Thermal management

● Semiconductor



● LED



Crucible coating

● Multi-Si ingot

Experimentals

Mixing

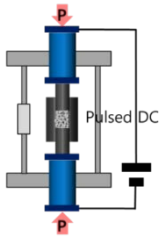
- SiC (1~3㎛) with additives (1wt% B_4C + 3wt% C)

Sintering

Pressureless sintering(Conventional sintering)

- Pressure : 270, 600MPa
- Temperature : 2070~2160℃
- Time : 1h
- Ar flow

Spark Plasma Sintering (SPS)



- Pressure : 30MPa
- Temperature : 1650~1800℃
- Time : 10min
- Vaccum

Effect of current on mechanical properties

Evaluation

- Phase, Microstructure
- Grain size
- Relative density
- Mechanical properties

XRD

FE-SEM

Vickers Hardness test

Density Measurement (Archimedes method)

Experimentals

Mixing

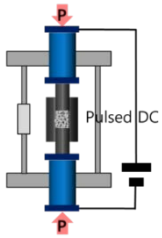
- Si_3N_4 (UBE E-10) with additives (2wt% MgO + 5wt% Y_2O_3)

Sintering

Pressureless sintering(Conventional sintering)

- Pressure : 270, 600MPa
- Temperature : 1800~2000℃
- Time : 1h
- Ar flow

Spark Plasma Sintering (SPS)



- Pressure : 50~150MPa
- Temperature : 1500~1800℃
- Time : 5~15min
- eating rate : 100~250℃/min

Effect of current on mechanical properties

Evaluation

- Phase, Microstructure
- Grain size
- Relative density
- Mechanical properties

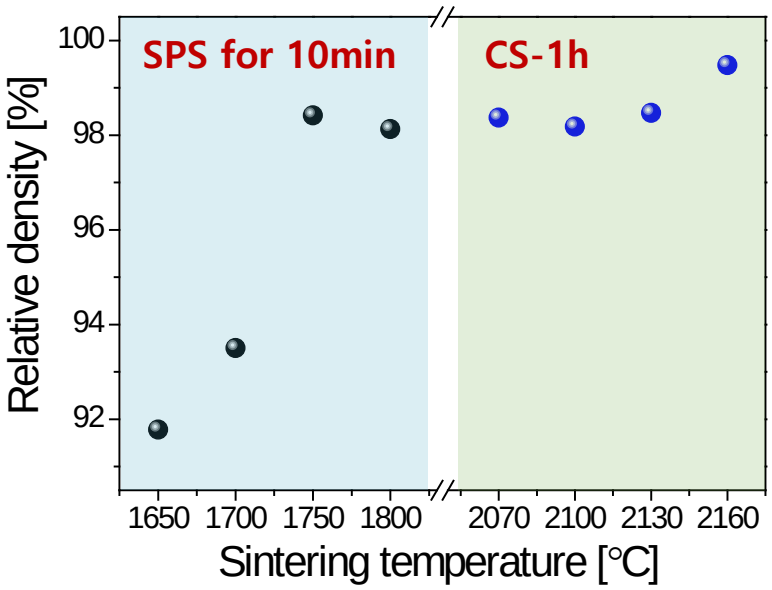
XRD

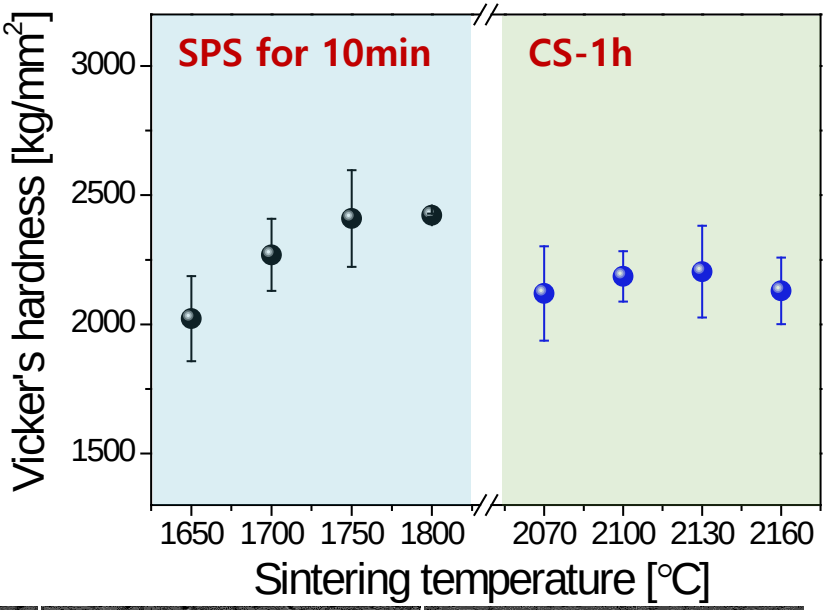
FE-SEM

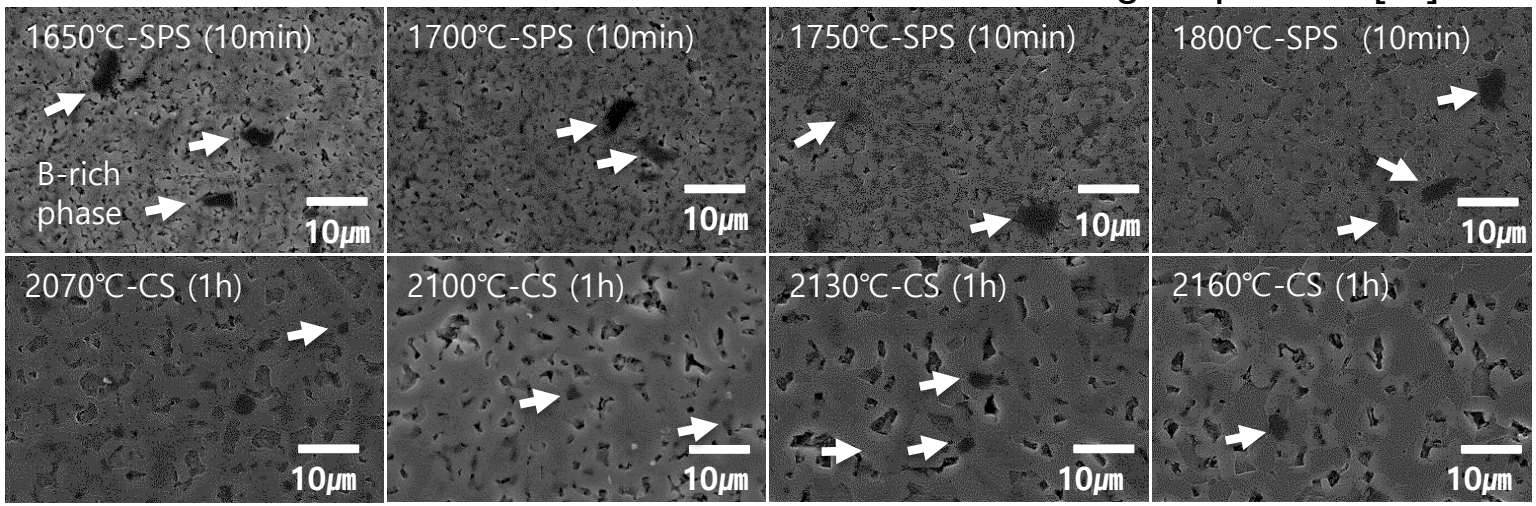
Vickers Hardness test

Density Measurement (Archimedes method)

Results

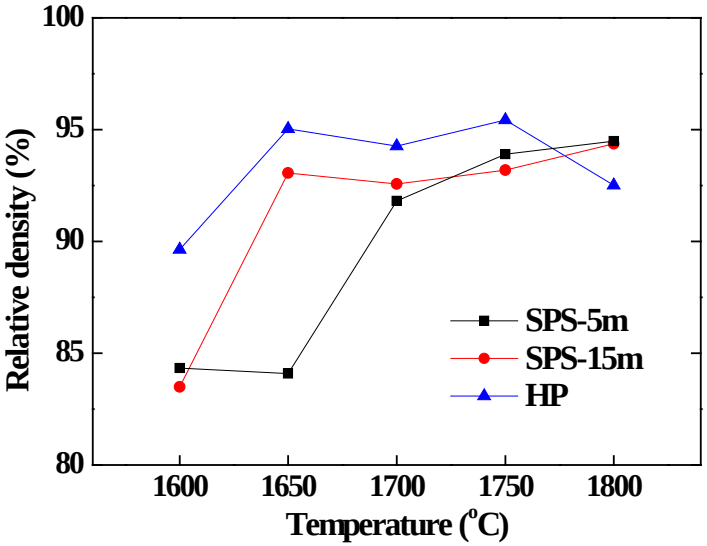


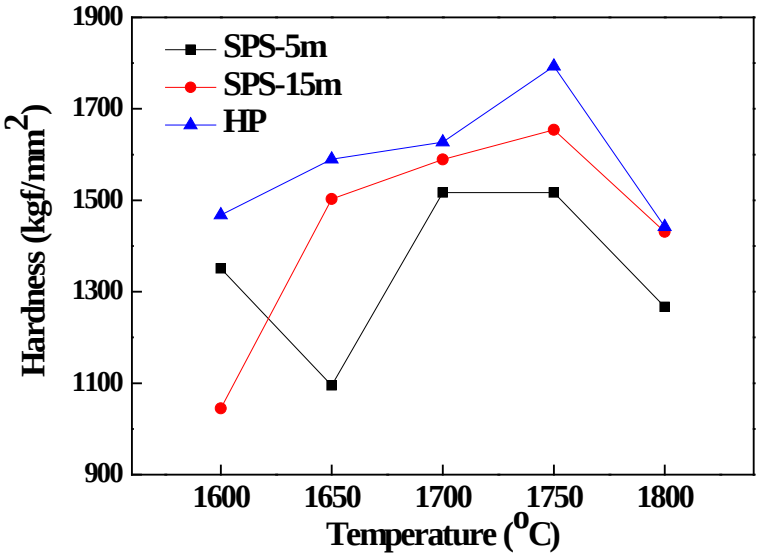


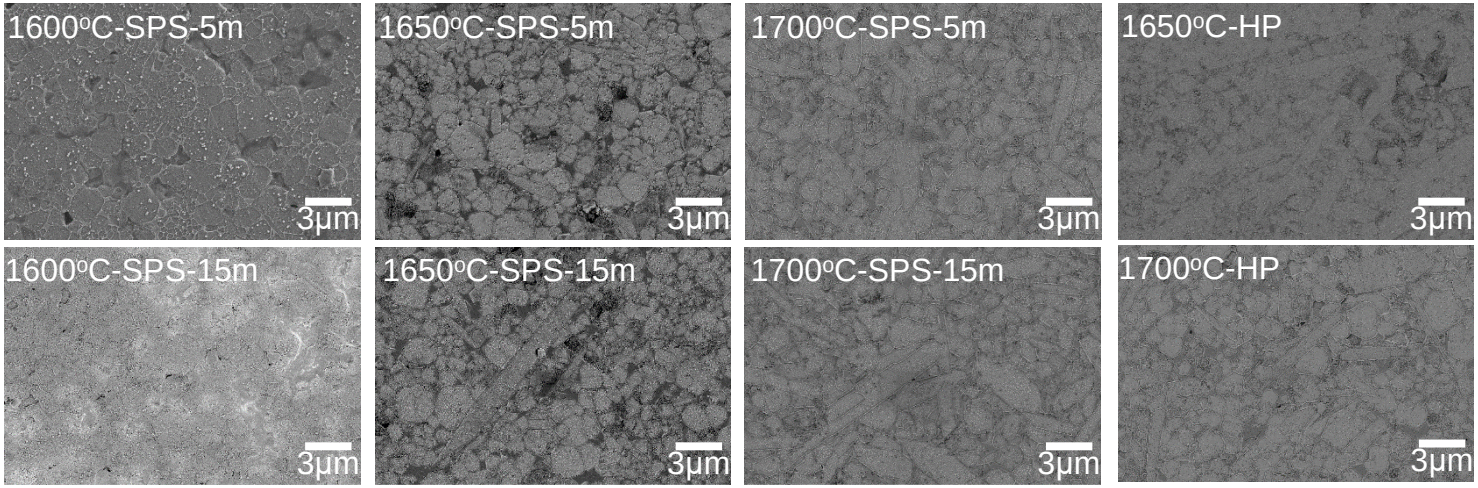


- **Sintering T ↑ → porosity ↓ → Density ↑**
- **SPS ; low T densification by current/heat effects**
  short time -> grain growth ↓
- **Hardness(SPS) >> Hardness(CS)**

Results







- **Sintering T ↑ → porosity ↓ → Density ↑**
- **No current effect : microstructure evolution, mechanical properties**

Discussion

- Silicon carbide
  - ✓Properties depend on sintering conditions
    -> temperature / time
  - ✓No special difference between SPS and CS
    -> paper published

Ceramics International
Volume 43, Issue 17, 1 December 2017, Pages 15332-15338

The effects of B_4C addition on the microstructure and mechanical properties of SiC prepared using powders recovered from kerf loss sludge

Jun-Young Cho [a], Tae-ho An [a], Sang-gu Ji [a], Youngseok Kim [b], Hyunick Shin [b], Sarah Wonjung Kim [c], Sung-Hwan Bae [d], Miyoung Kim [a], Chan Park [a, e]

- Silicon nitride
  - ✓Properties depend on sintering conditions
    -> temperature / time
  - ✓HPed properties are relative higher than SPSed

PART 2.

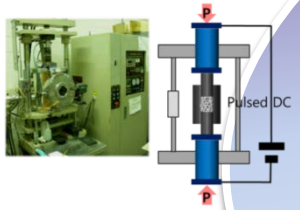
RECYCLED KERF LOSS SLUDGE SIC AND DOMESTIC PRODUCTION SI3N4 SINTERING PROPERTIES

Intro

➢ Recycled kerf loss sludge SiC and Domestic production Si3N4 Sintering properties

Evaluation mechanical properties with microstructure

Sintering with various process parameters



- Temperature
- Time
- Pressure
- Heating rate

- Phase analysis
- Relative density
- Microstructure
- Machnical properties

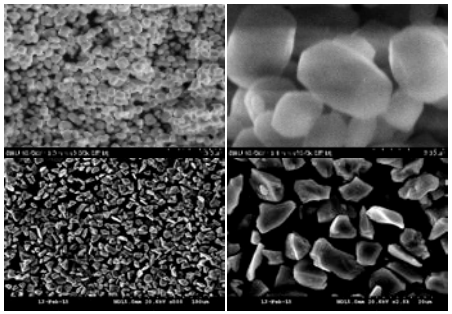
Enhancement density and properties with microstructure control

Hard-to-sinter powder

Recycled and Domestic production powder

Recyled SiC

Domestic powder



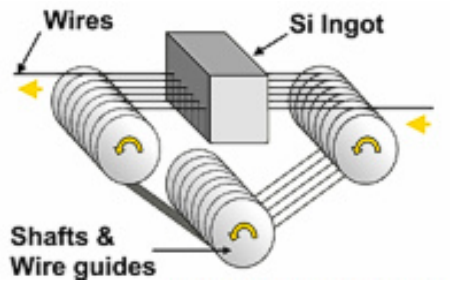
Sintering database

- Full-density with SPS
- Comparison Domestic and overseas powder
- Database

SPS

Recycled silicon carbide

➢ Recycling technique



Solid phase separation

Classification

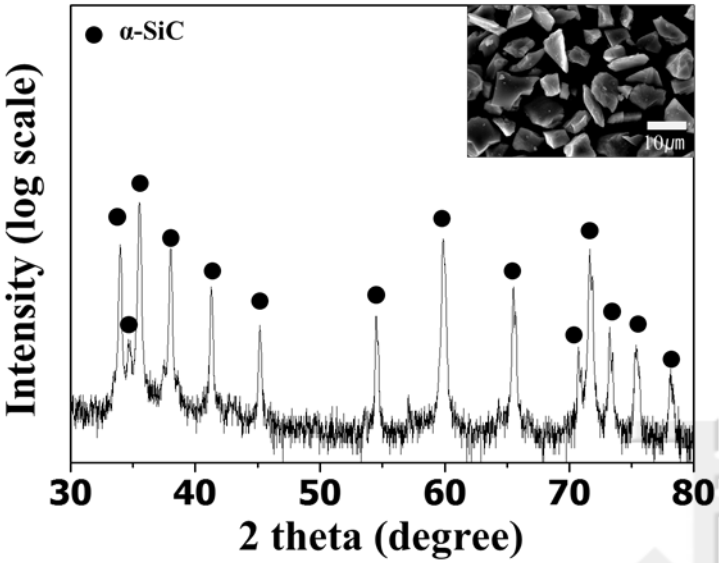
www.quantum14.com/english/g5.html

SiC powder

Cutting wire ; SiC abrasive

Composition	SiC (%)	Recycled SiC (%)
SiC (%)	99	99.2
Free-SiO2 (%)	0.75	0.51
Free-Si (%)	0.05	0.21
Free-C (%)	0.20	<0.01
Fe (ppm)	50	303
Al (ppm)	250	28
Ni (ppm)	<10	25
V (ppm)	70	19
Na (ppm)	<100	23
Ca (ppm)	20	79
Ti (ppm)	200	50
Mg (ppm)	<100	10
K (ppm)	20	15

Recycled SiC



Production technique of silicon nitride

- Carbothermal reduction

  : $3SiO_2 + 6C + 2N_2 \rightarrow Si_3N_4 + 6CO$ (1300~1500 °C)

- Vapor phase reaction

  : $3SiCl_4 + 16NH_3 \rightarrow Si_3N_4 + 12NH_4Cl$ (1300~1500 °C)

- Direct niridation

  : $3Si + 2N_2 \rightarrow Si_3N_4$ (1300~1500 °C)

- Imide decomposition

  - Step 1: $SiCl_4 + 6NH_3 \rightarrow Si(NH)_2 + 4NH_4Cl$ (-50~0 °C, in solvent)
  - Step 2: Solvent removal
  - Step 3: $3Si(NH)_2 \rightarrow$ amorphous-$Si_3N_4 + 2NH_3$ (1000 °C)
  - Step 4: $Si_3N_4 \rightarrow$ crystal-Si_3N_4 (1300~1500 °C)

Method	Quality	Purity	Cost	Productivity	Company
Carbothermal reduction	X	X	O	O	
Vapor phase reaction	O	O	△	X	
Direct nitridation	△	△	O	O	DENKA H.C.Starck
Imide decomposition	O	O	X	O	UBE
LT vapor-phase reaction	O	O	△	O	

OCI company

New synthesis method

High quality

Low cost

Low-temperature vapor-phase reaction

- Step 1: $SiCl_4 + 6NH_3 \rightarrow Si(NH)_2 + 4NH_4Cl$ (25 °C)
- Step 3 $3Si(NH)_2 \rightarrow$ amorphous-$Si_3N_4 + 2NH_3$ (1000 °C)
- Step 4: $Si_3N_4 \rightarrow$ crystal-Si_3N_4 (1300~1500 °C)

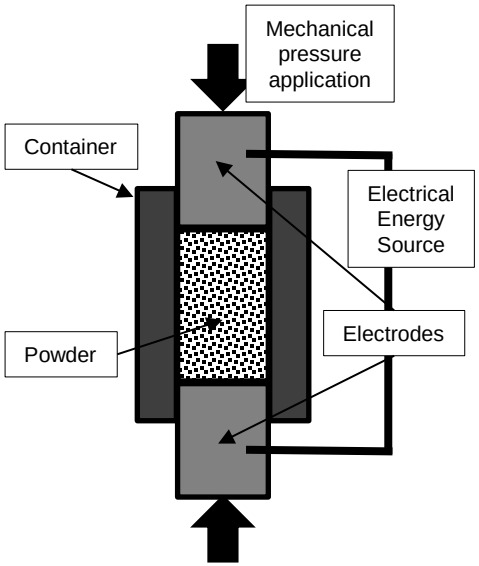
PART 3.

EFFECT OF ELECTRIC CURRENT ON SILICON NITRIDE CERAMIC ON SINTERING

Effect of electric current on Silicon nitride ceramic on sintering

➢ Background

✓SPS(Spark plasma sintering) Apparatus and Features



- Apparatus
  - Mechanical press
  - Electrical energy supply
  - Electrodes
  - Container (mold/die)
  - Material (powder form)
- Features
  - Fast heating rate
  - Low sintering temperature
  - Short holding time

✓SPS Advantages and Application

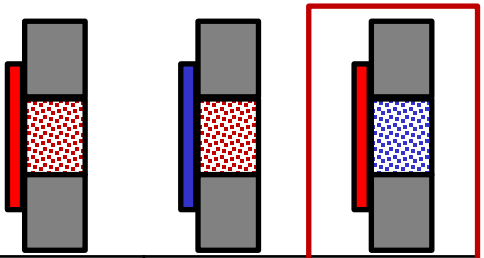
- Full densification with limited, or even inhibited grain growth
- Prevent undesirable phase transformations/reaction in the initial materials
- Every materials can sinter (metal/ceramic/composite)

Materials Science and Engineering: R: Reports Volume 63, Issues 4–6, 12 February 2009, Pages 127-287

Effect of electric current on Silicon nitride ceramic on sintering

➢ Background

✓Possible mold set-up on conductivity of ceramic materials

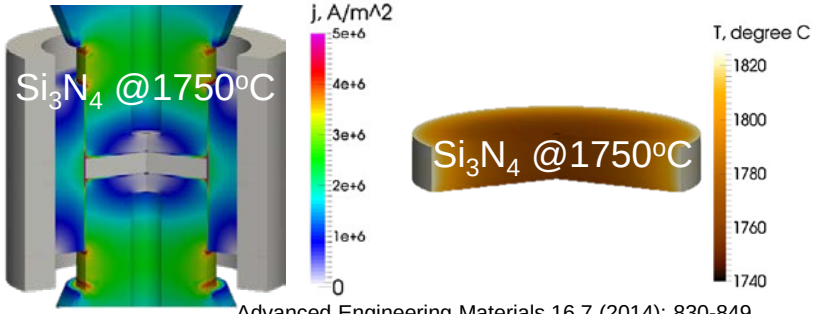


	Case 1	Case 2	Case 3
powder	conducting	conducting	insulating
container	conducting	insulating	conducting

- Conductive ceramic materials
  - Conducting/insulating mold can be used
  - Conducting mold
    -> general SPS
  - Insulating mold
    -> SPS with high current density
- Insulating materials
  - Only conducting mold can be used

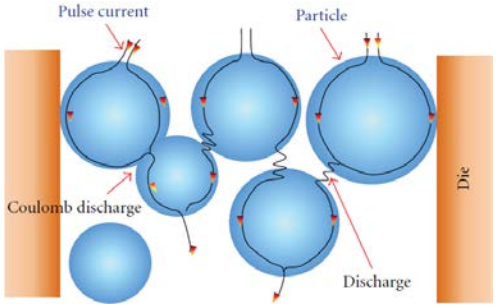
✓Effect of the current on ceramic sintering

- Simulation results



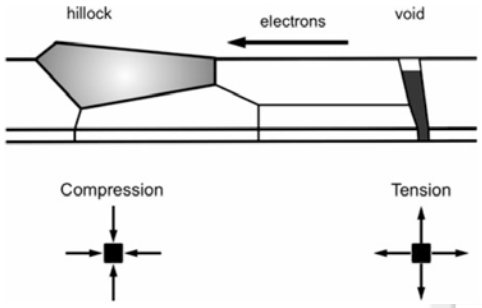
Advanced Engineering Materials 16.7 (2014): 830-849

- Thermal effect



Sintering Applications. InTech, 2013.

- Electrical effect



J. Mat. Res. 12 (1997) p.2027-2037

-> Material transfer can thermodynamically and kinetically enhance

J. Am. Ceram. Soc. 74 [6] 1217-25 (1991)

Effect of electric current on Silicon nitride ceramic on sintering

➢ Background

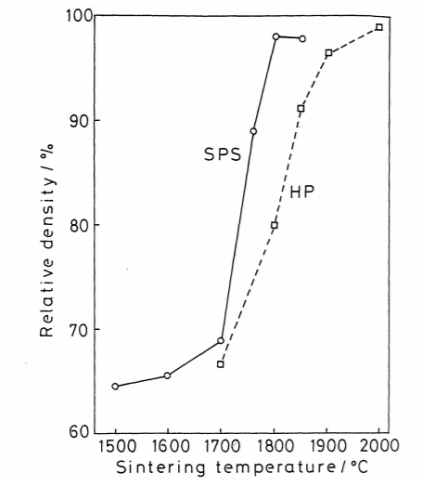
✓Comparison HP vs SPS

- Effect of SPS on densification and mechanical properties of SiC

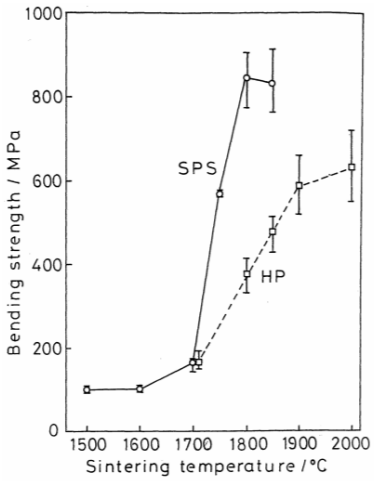
Materials: SiC + 5wt% Al_2O_3 + 2wt% Y_2O_3

Conditions: 1800°C, 30Mpa and 5min

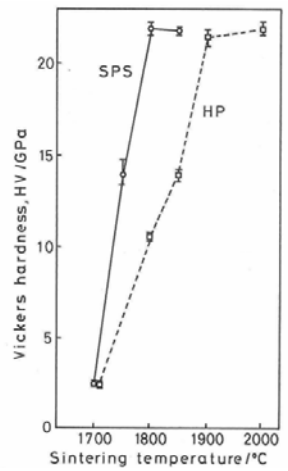
Journal of the Ceramic Society of Japan 103 [7] 1995



Densification behavior of silicon carbide by SPS and HP



Effect of sintering temperature on bending strength @RT



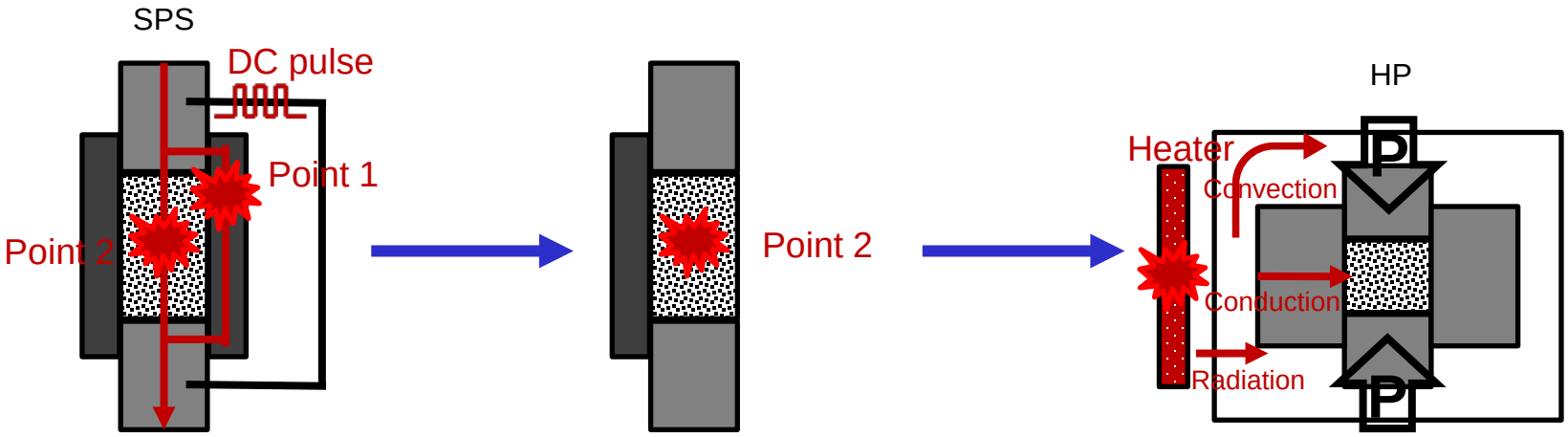
Effect of sintering temperature on Vickers hardness

-> The results suggest that the inside temperature of the sintered bodies during SPS was higher than the measured temperature

Effect of electric current on Silicon nitride ceramic on sintering

- Purpose
  - ✓To investigate the effect of current on sintering

- Experimental set-up
  - ✓Thermal effect - In-situ temperature measurement
  - ✓Electrical effect – Microstructure analysis

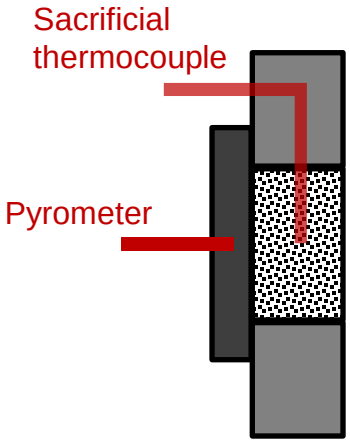


-> Comparison SPS and HP process (existence of electric current)

Effect of electric current on Silicon nitride ceramic on sintering

➢ Experimental details

✓In-situ temperature measurement



Advanced Engineering Materials 16.7 (2014): 830-849

✓Thermocouple

- Type C

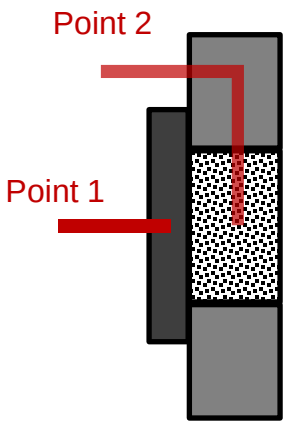
Connectors

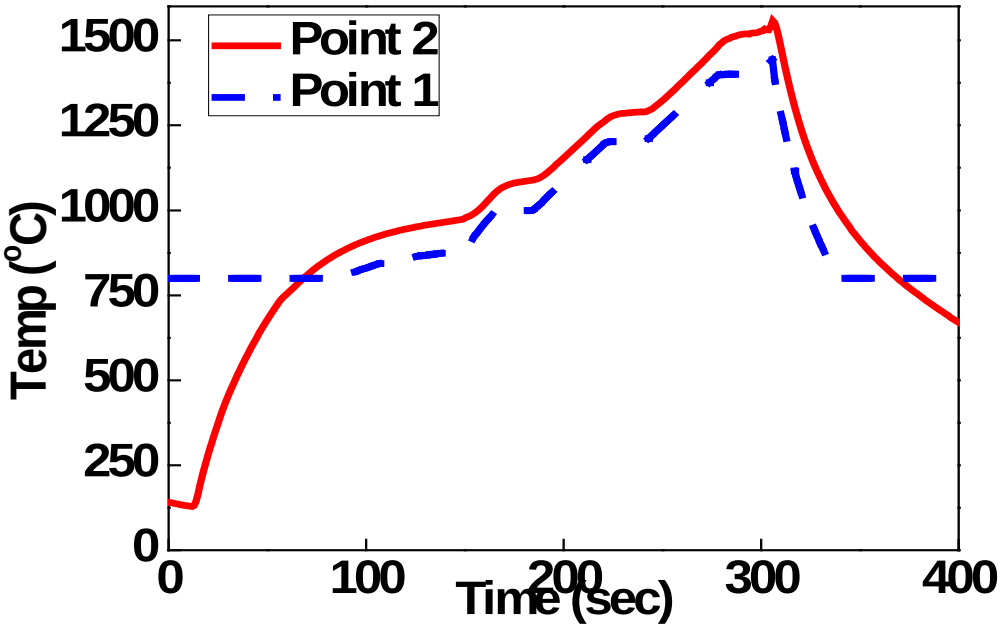
ANSI Code	ANSI MC 96.1 Colour Coding Thermocouple	Extension	Alloy Combination		Comments Environment	Maximum T/C Grade Temp.	EMF (mV) Over Max. Temp.	IEC 584-3 Colour Coding Thermocouple	Intrinsically	IEC Code
G* (W)	NONE ESTABLISHED		TUNGSTEN W	TUNGSTEN-26% RHENIUM W-26% Re	Vacuum, Inert, Hydrogen. Beware of Embrittlement. Not Practical Below 399°C (750°F). Not for Oxidising Atmosphere	0 to 2320°C 32 to 4208°F	0 to 38.564	NO STANDARD USE ANSI COLOUR CODE		G (W)
C* (W5)	NONE ESTABLISHED		TUNGSTEN-5% RHENIUM W-5% Re	TUNGSTEN-26% RHENIUM W-26% Re	Vacuum, Inert, Hydrogen. Beware of Embrittlement. Not Practical Below 399°C (750°F) Not for Oxidising Atmosphere	0 to 2320°C 32 to 4208°F	0 to 37.066	NO STANDARD USE ANSI COLOUR CODE		C (W5)
D* (W3)	NONE ESTABLISHED		TUNGSTEN-3% RHENIUM W-3% Re	TUNGSTEN-25% RHENIUM W-25% Re	Vacuum, Inert, Hydrogen. Beware of Embrittlement. Not Practical Below 399°C (750°F)–Not for Oxidising Atmosphere	0 to 2320°C 32 to 4208°F	0 to 39.506	NO STANDARD USE ANSI COLOUR CODE		D (W3)

Effect of electric current on Silicon nitride ceramic on sintering

➢ Results

✓The actual temperature in power during SPS





- Point 1 can measure temperature above 800°C
- Point 2 temperature is higher thank Point 1 in all range

-> Pyrometer and thermocouple temperature calibration should be done at same position

Structural and Electrical Characterization of Sintered Silicon Nitride Ceramic. *Materials Sciences and Applications*, *2*(07), 738.

Effect of electric current on Silicon nitride ceramic on sintering

- Electrical effect of SPS
  - ✓The actual temperature in power during SPS
    - * Temperature of SPS and HP should be same

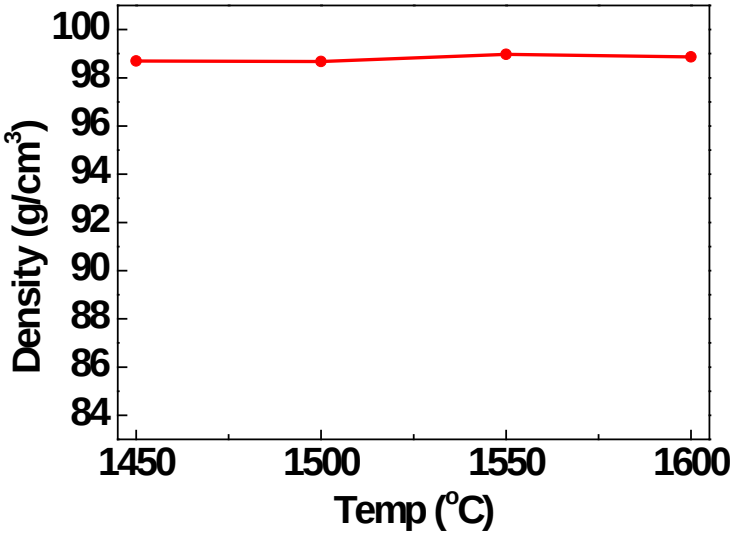
In progress…

Addtional

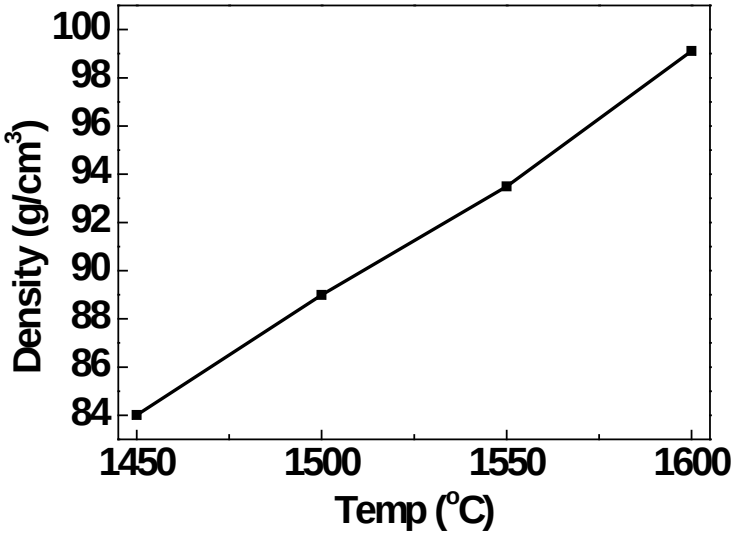
- Si_3N_4 sintering using SPS
  - ✓Temperature range: 1400-1600°C (with full density)
  - ✓Actual temperature: 1600~1850°C (melting T: 1900°C) -> HP conditions

maximum

SPS process



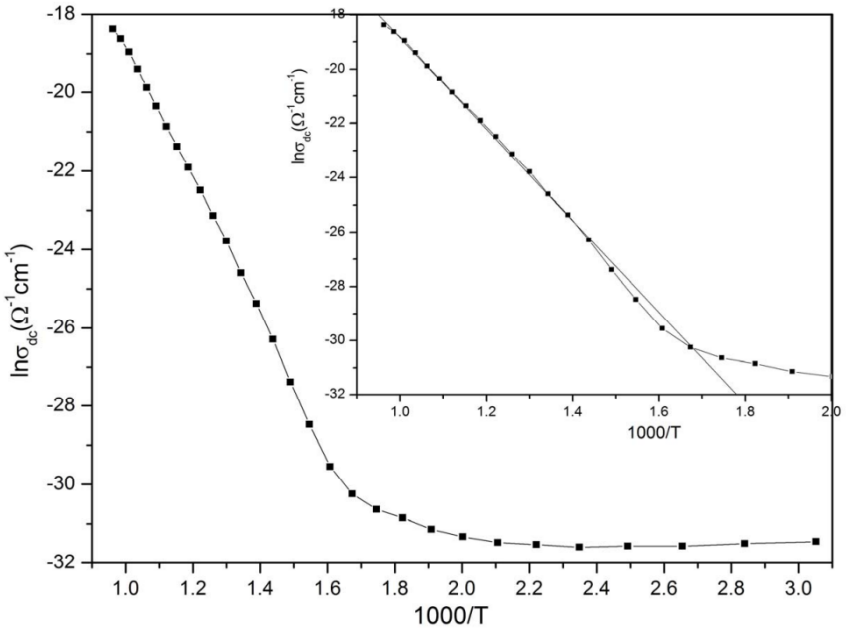
HP process



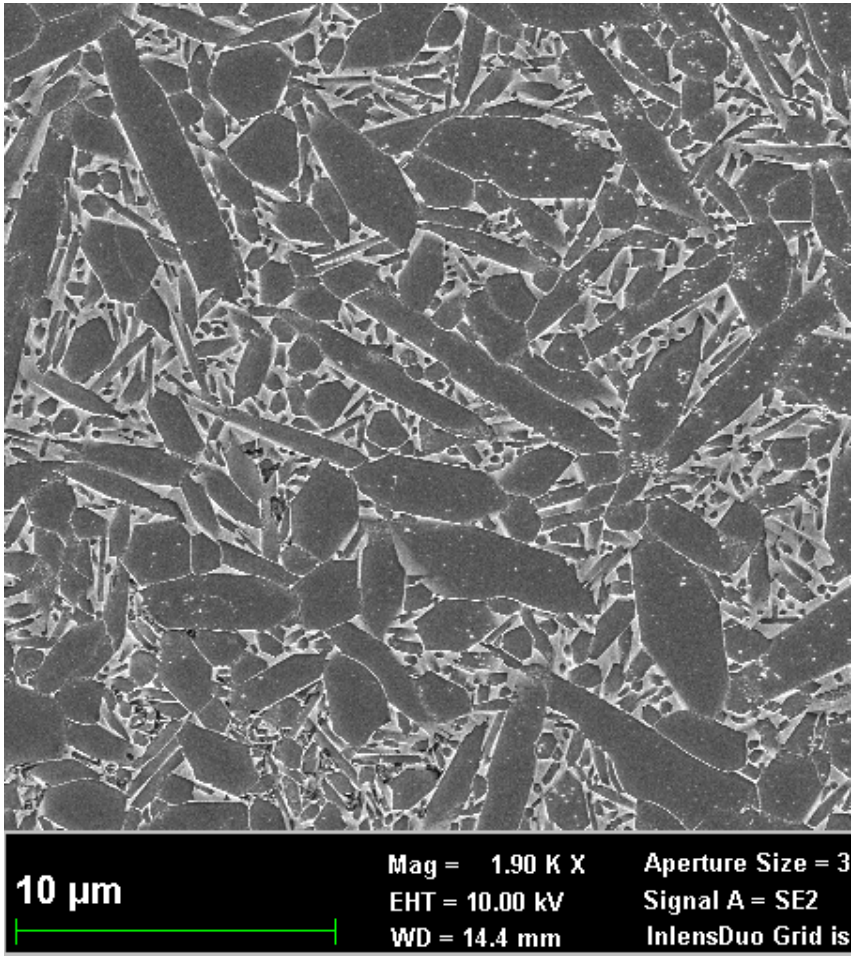
- Same temperature conditions will be secured
- Other conditions also will be same (pressure, time and etc.)

Additional

- Electrical property of Si_3N_4 ceramic / Etching



✓Data: resistance of Si3N4 on temperature



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Question or Comment