Institute of Materials Research, SAS

Institute of Inorganic Chemistry , SAS

Development of SiC based nanocomposites with enhanced electrical conductivity.

Richard Sedlák, Martin Fides, Alexandra Kovalčíková, Roman Bystrický, Miroslav Hnatko, Maciej Rutkowski

Pavol Hvizdoš

AGH

AGH University of Science and Technology

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Outline

- Introduction – SiC based ceramics
- Motivation – toughness, electric conductivity, EDM
- Challenges – fabrication, characterization, results
  - SiC-GPL
  - SiC-CNT
  - SiC-TiNbC

SiC based ceramics

Properties of SiC:

- ↑ resistance to corrosion and oxidation
- ↑ resistance to thermal shock
- ↑ low densities (3,21 g.cm^{-3}),
- ↑ high strength (~ 550 MPa)
- ↑ hardness (HV~21–27 GPa)
- ↓ **Electrical conductivity (~2,4–3,3 eV** - semi-conductive material **)**



Challenge of SiC machining

- SiC – very hard (HV~21-27 GPa)

⇓

costly final machining

⇓

electrical discharge machining (EDM)

- SiC - semiconductor

(for EDM $\sigma > 10^{-3}$ S·mm^{-1})

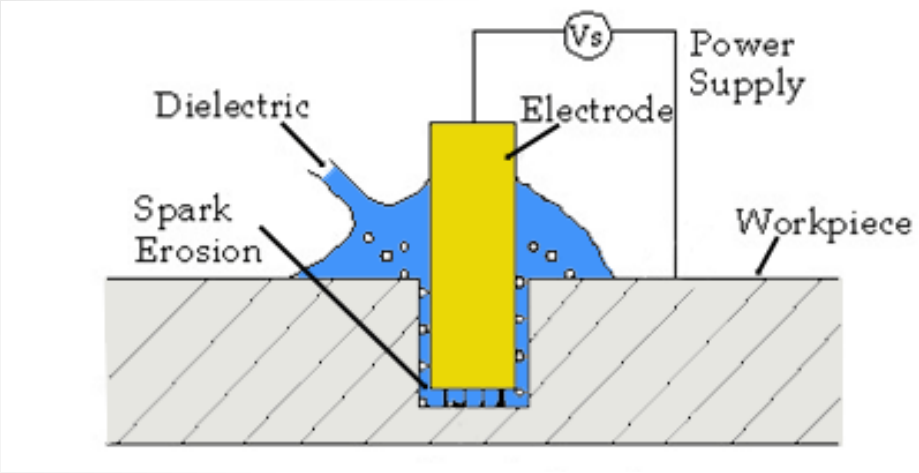
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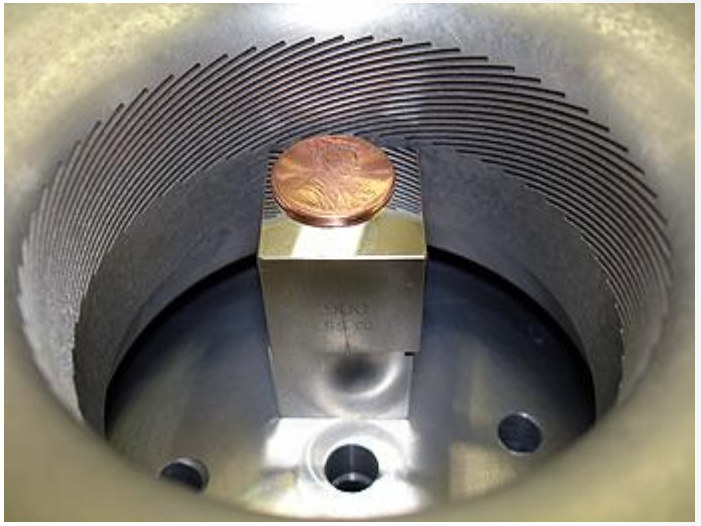
increase of conductivity

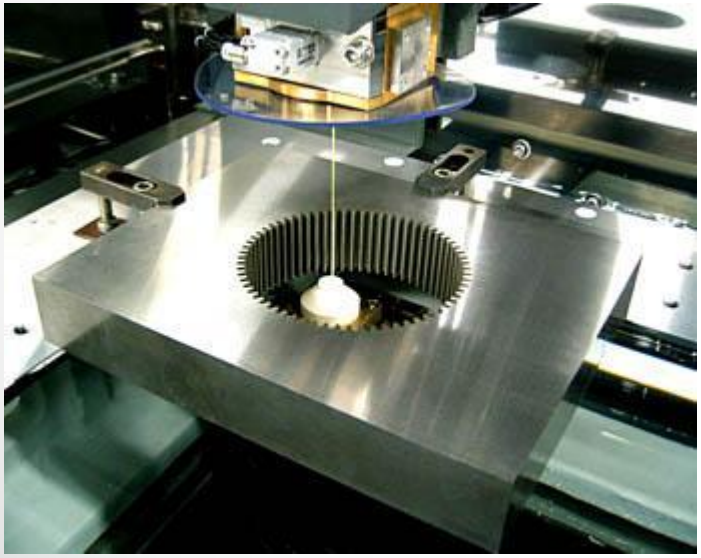
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addition of el. conduct. phases with retaining mechanical properties

Electric discharge (spark) machining



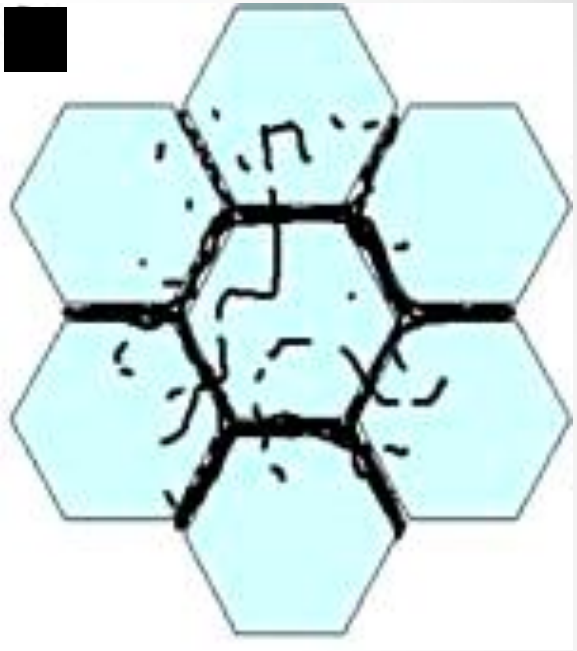


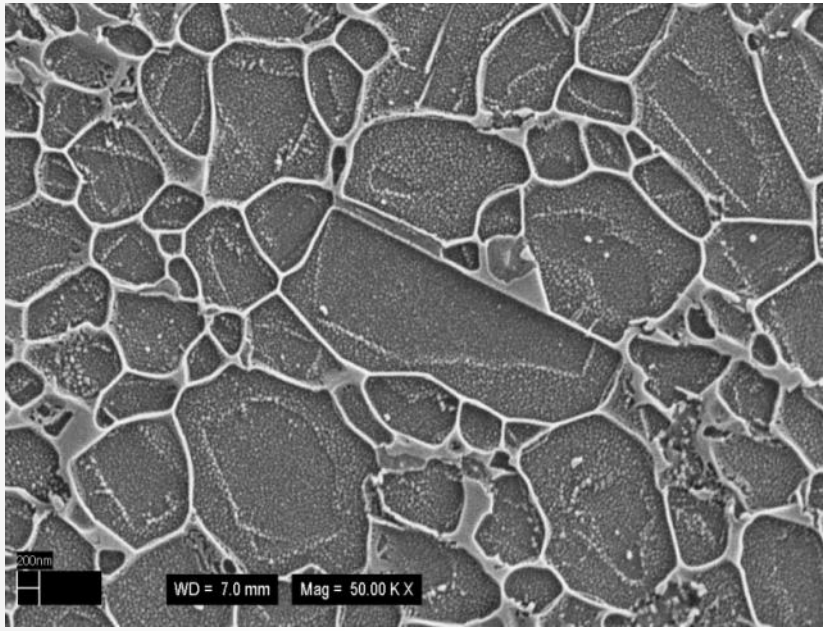




Increase of electrical conductivity

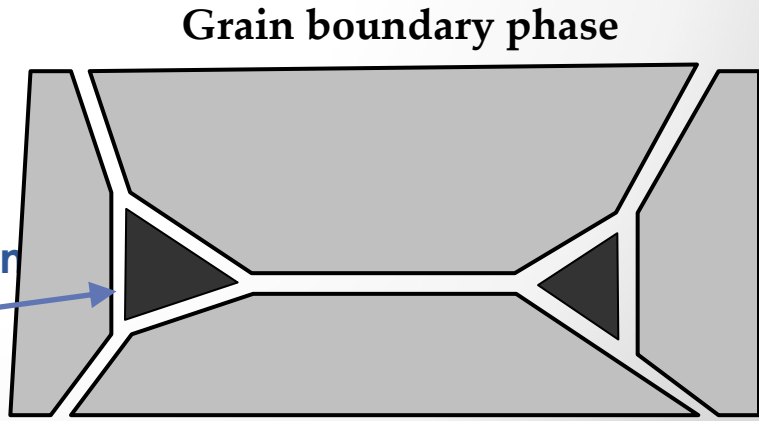
Appropriate distribution of carbon nanophases (graphene multilayers GPL and nanotubes CNT) – possibility of retaining or increasing of basic properties + enhancing functional and electrical ones.





Modification of SiC grain boundary phase by electrically conductive phases (Ti-NbC based) in non conductive matrix

(Ti_5Si_3, Nb_5Si_3, TiC, $NbTi_{(ss)}$, $(NbTi)C_{(ss)}$)



AIM

- to prepare electrically SiC based composites with

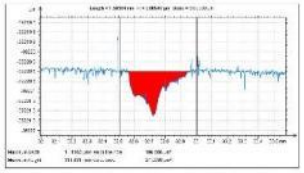
1. Graphene multilayers (GPL)
2. CNTs (in-situ deposited)
3. TiNbC based additives

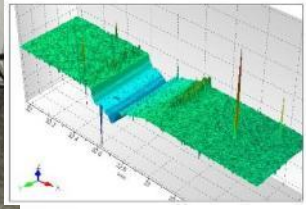
- to characterize them in terms of microstructure, basic mechanical, electrical and technological properties

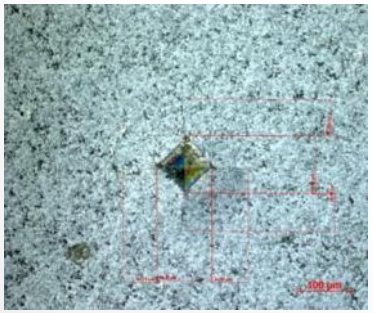
Characterization

- Microstructure
- Hardness (nanohardness)
- Indentation toughness
- Electric conductivity
- *Friction and wear*
- *Cutting (SiC-TiNbC)*











SEM - FIB



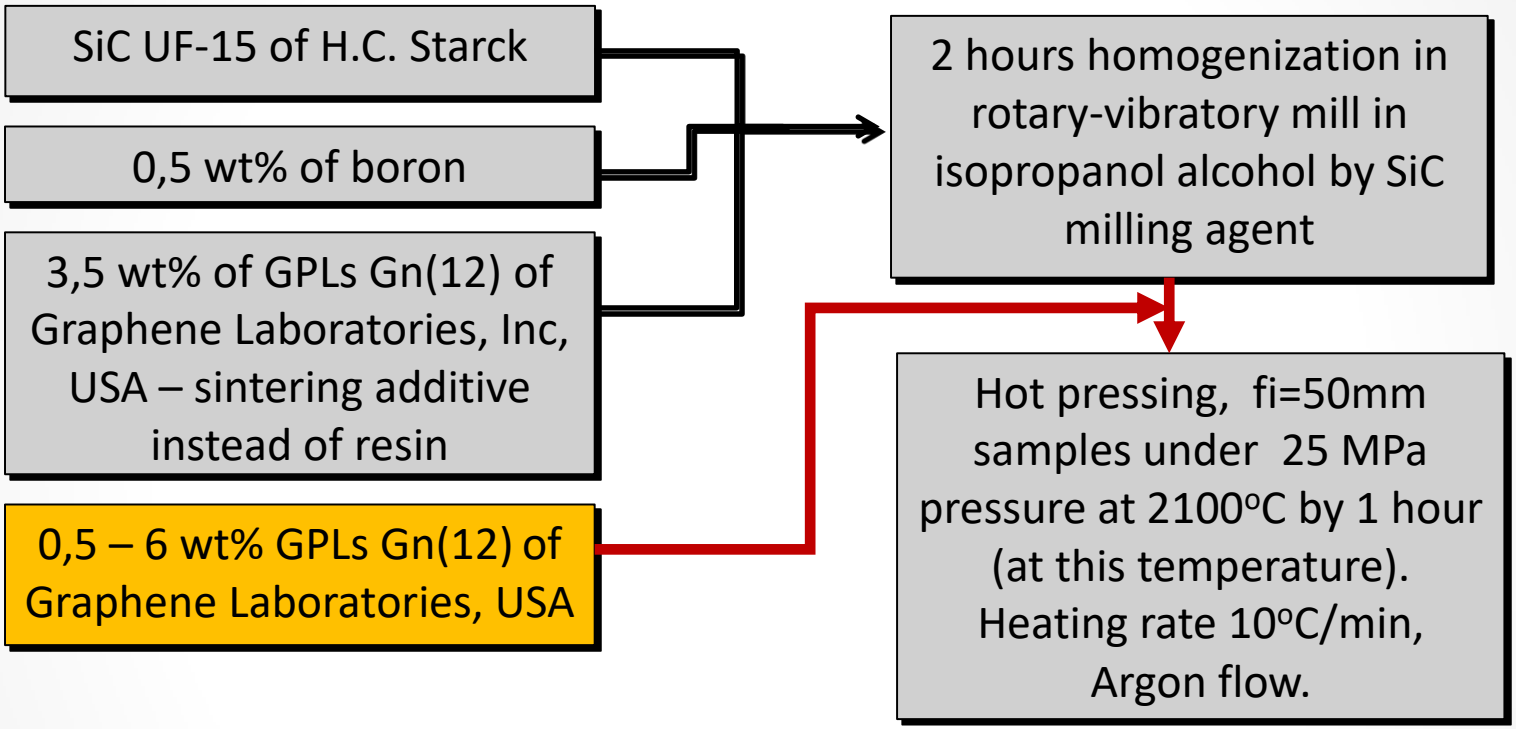


Nanohardness – Berkovich tip, 500, 250, 100, 10 mN

$$HV = \frac{1.8544 \cdot P}{d^2}$$

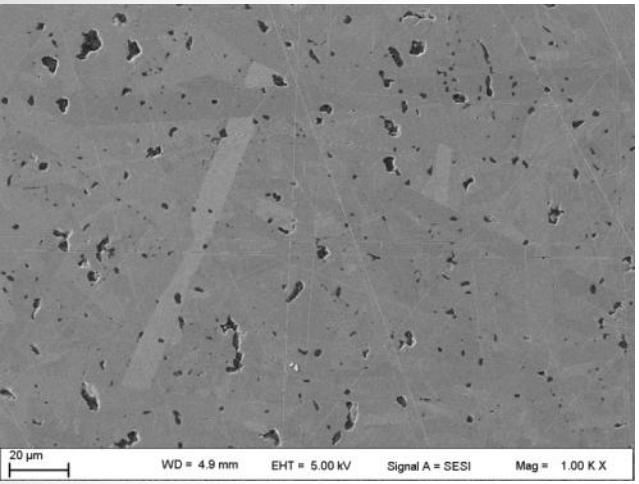
$$K_{IC} = 0.016 \cdot \left(\frac{E}{H}\right)^{\frac{1}{2}} \cdot \left(\frac{P}{c^{\frac{3}{2}}}\right)$$

1. SiC-GPL fabrication

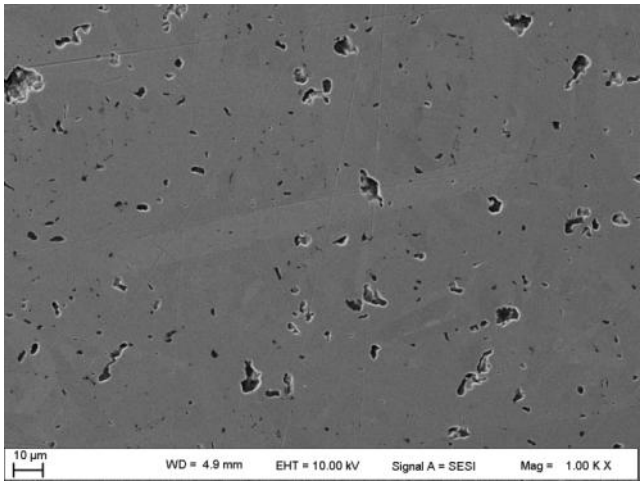


Resulting materials: **GPL0, GPL0.5, GPL1 GPL2, GPL4, GPL6**

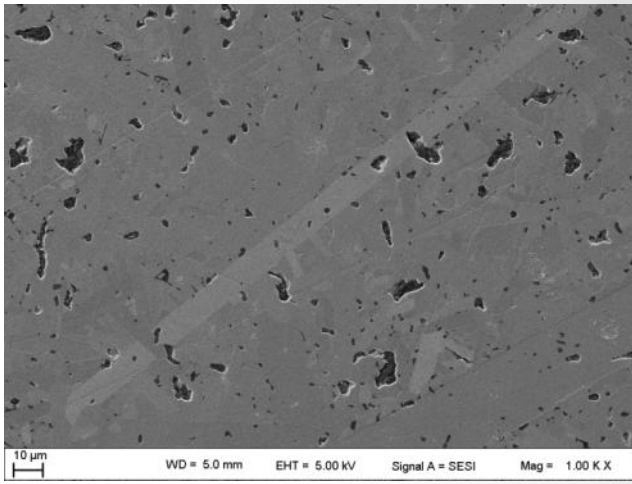
SiC-GPL
Microstructure



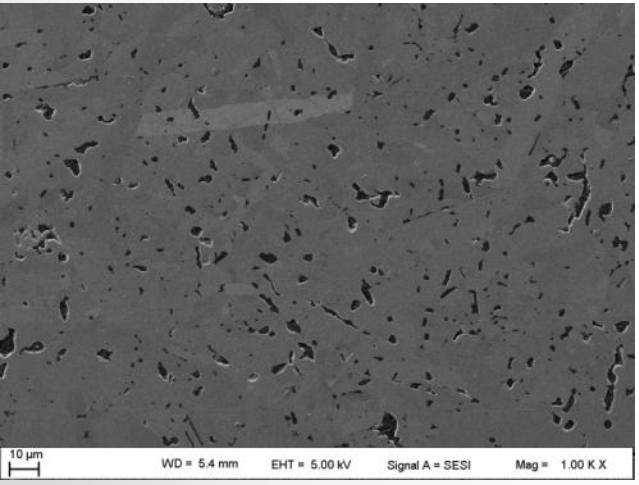
GPL 0



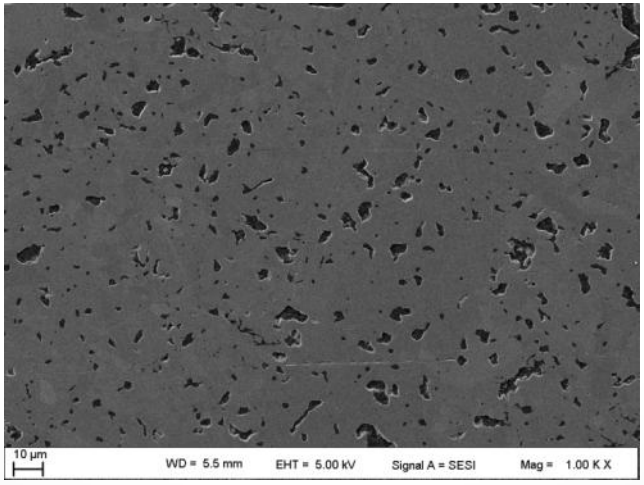
GPL 0.5



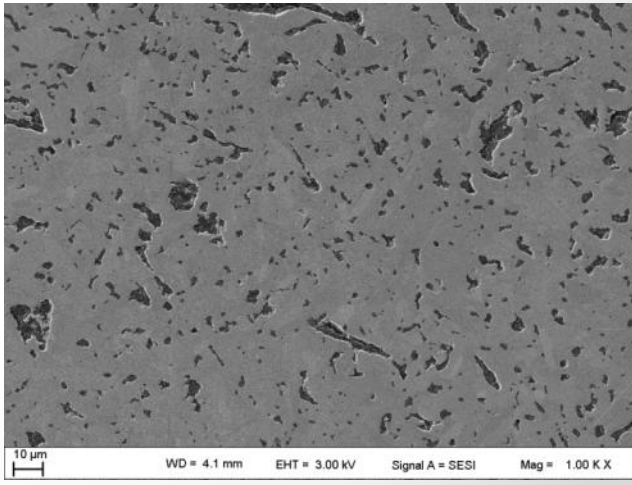
GPL 1



GPL 2

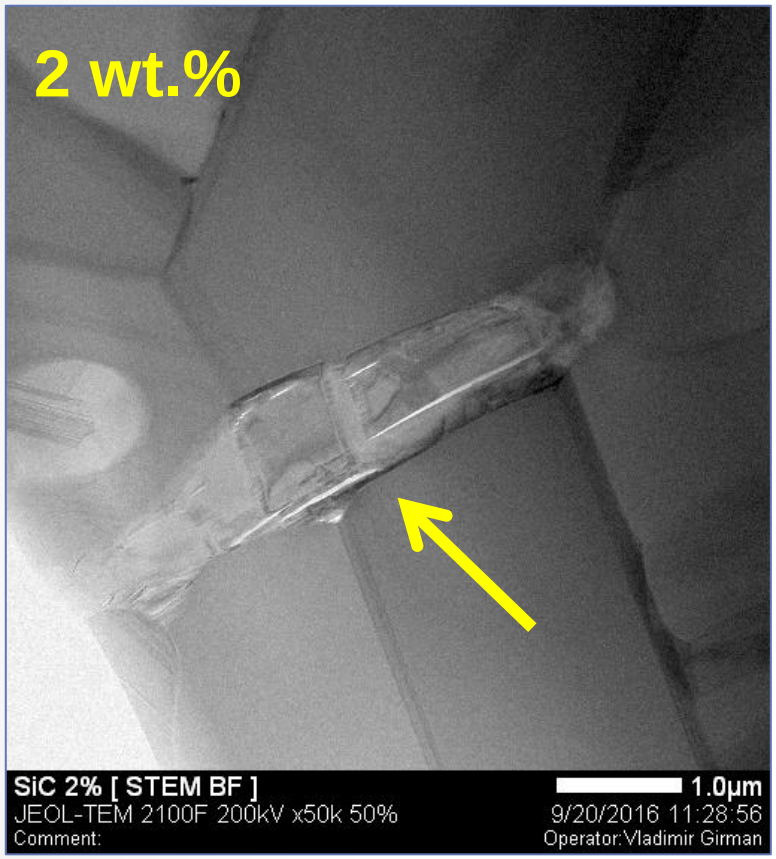


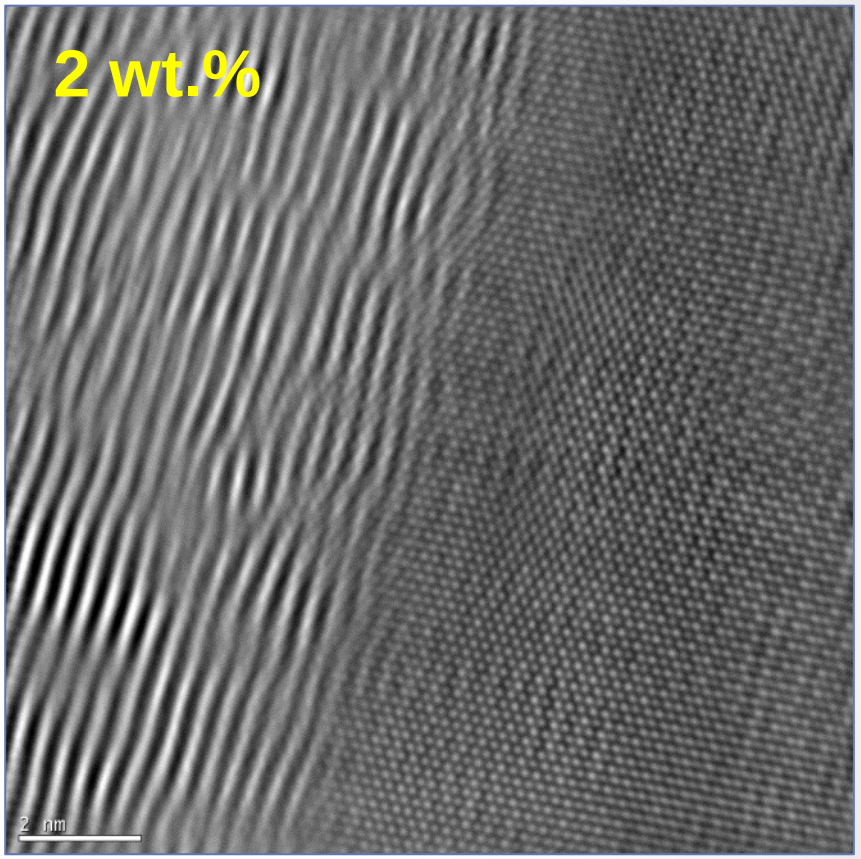
GPL 4



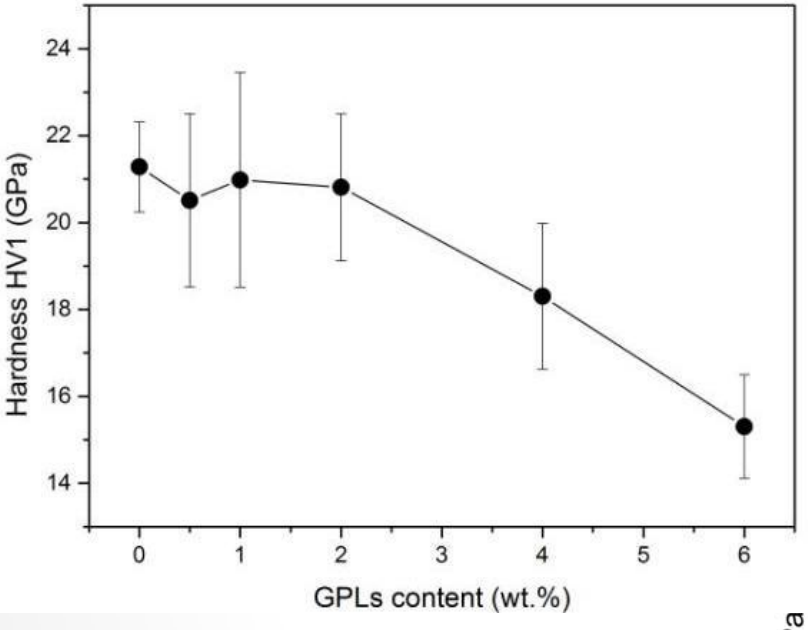
GPL 6

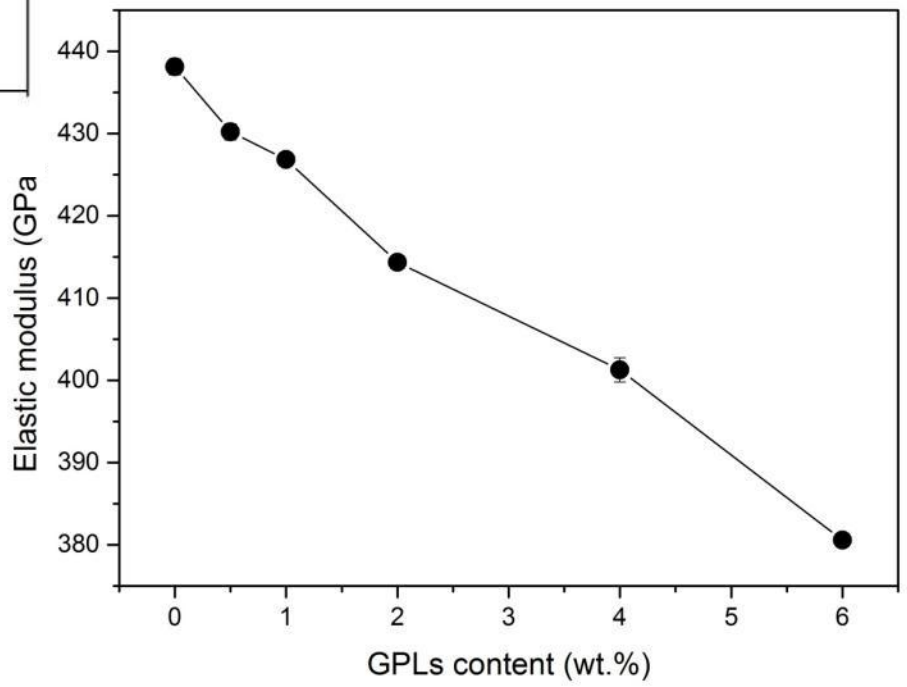
SiC-GPL
Microstructure - TEM



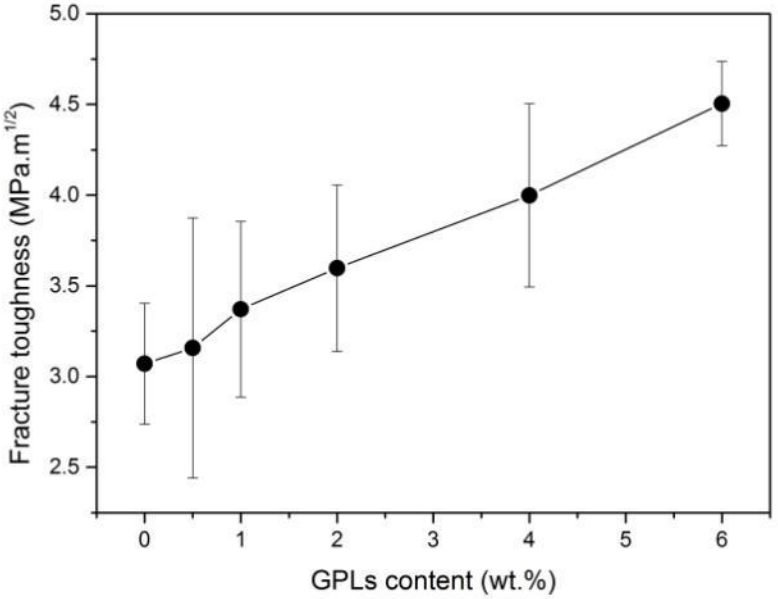


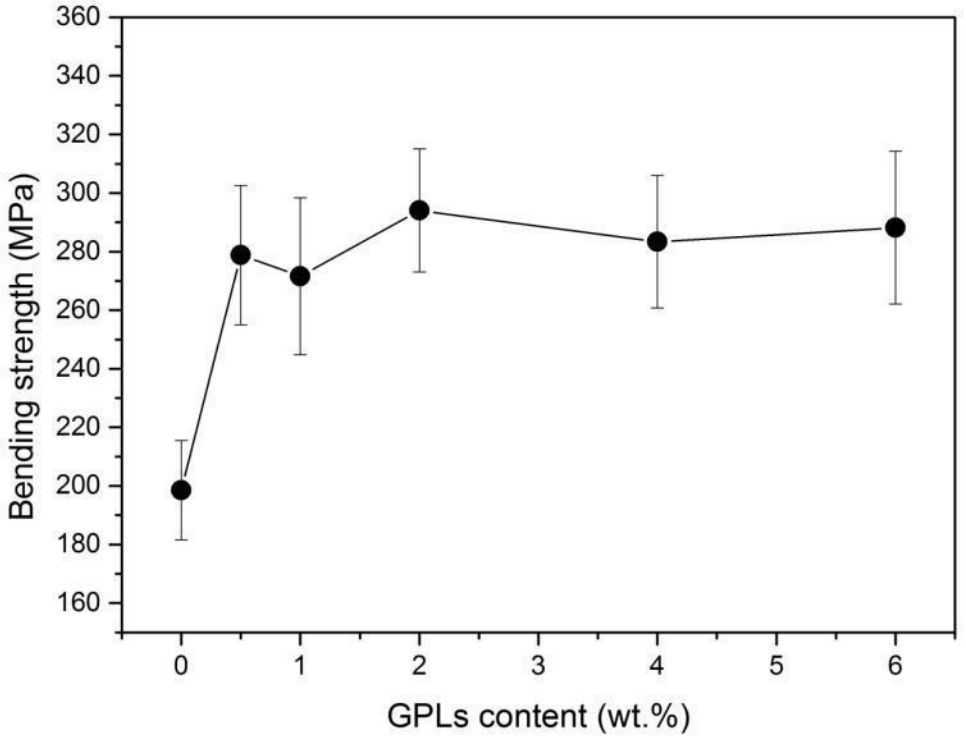
SiC-GPL
hardness and elasticity



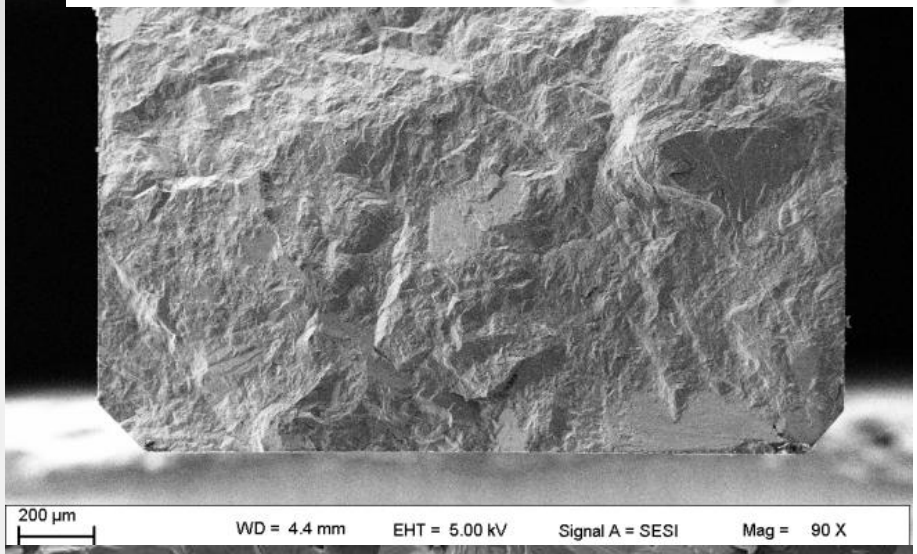


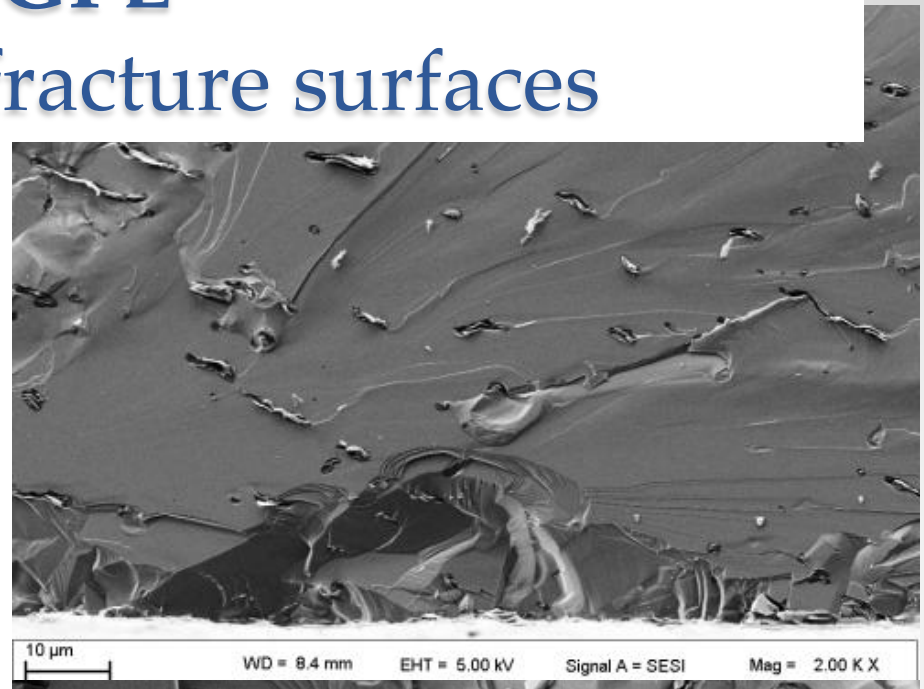
SiC-GPL
indentation toughness and bending strength

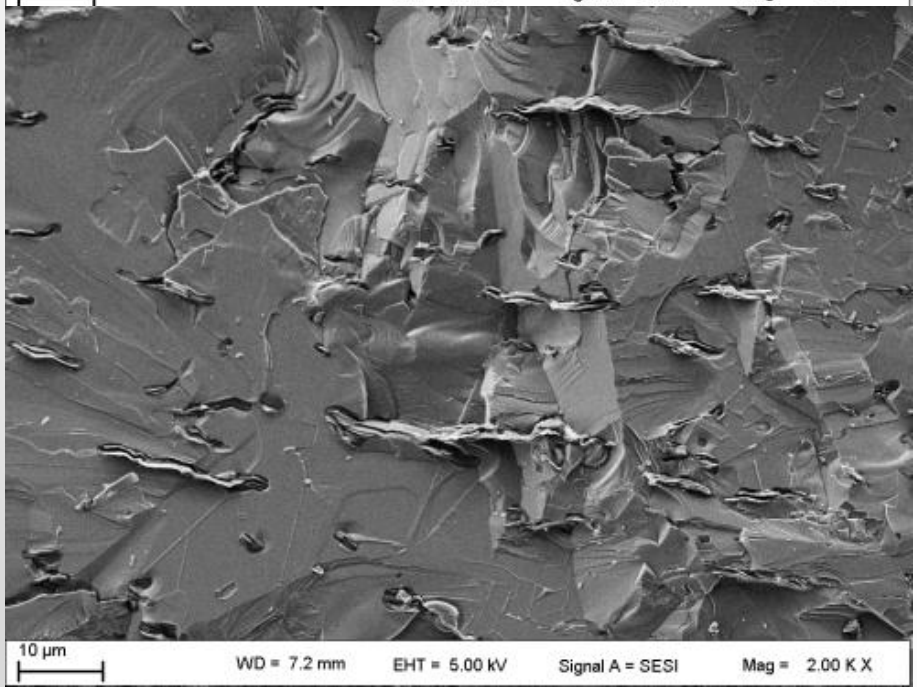


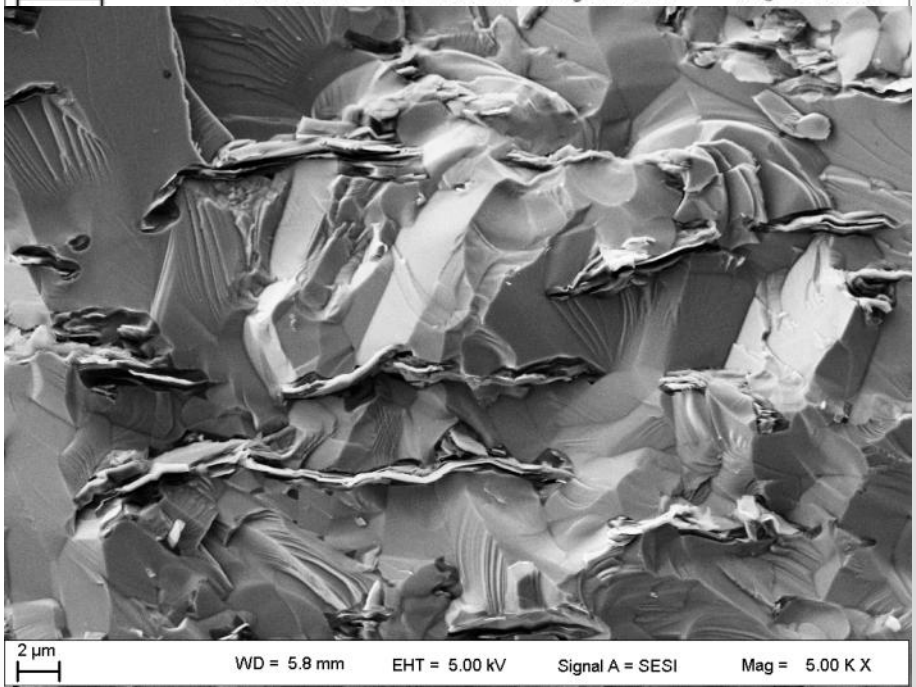


SiC-GPL
fractography – fracture surfaces

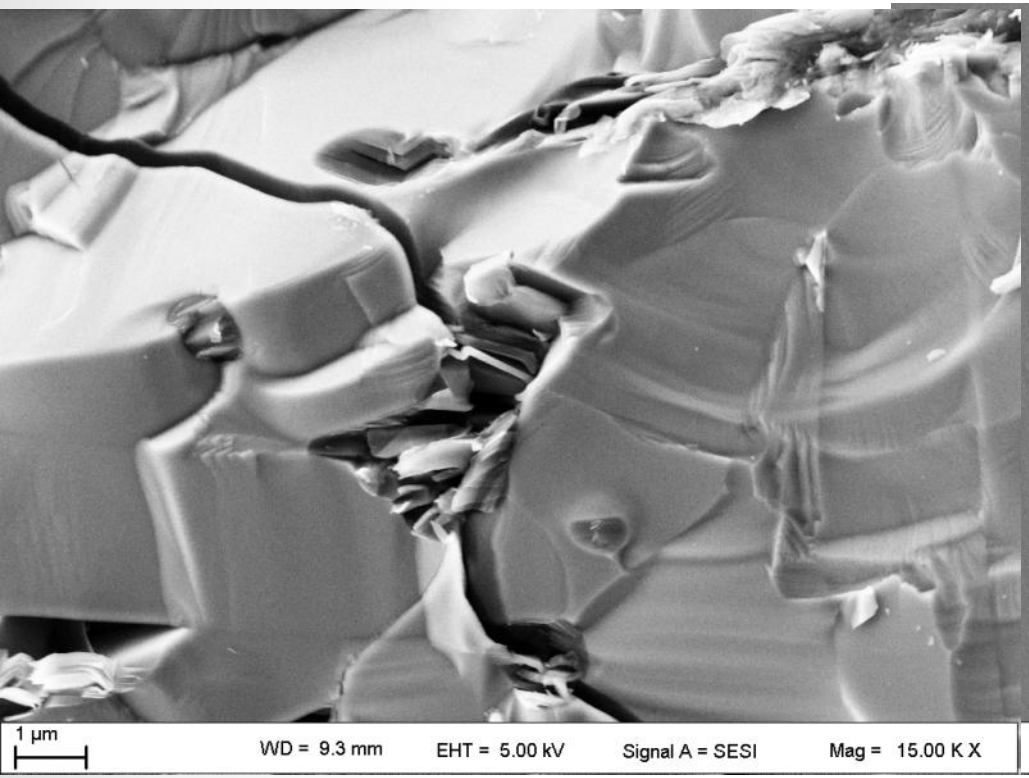


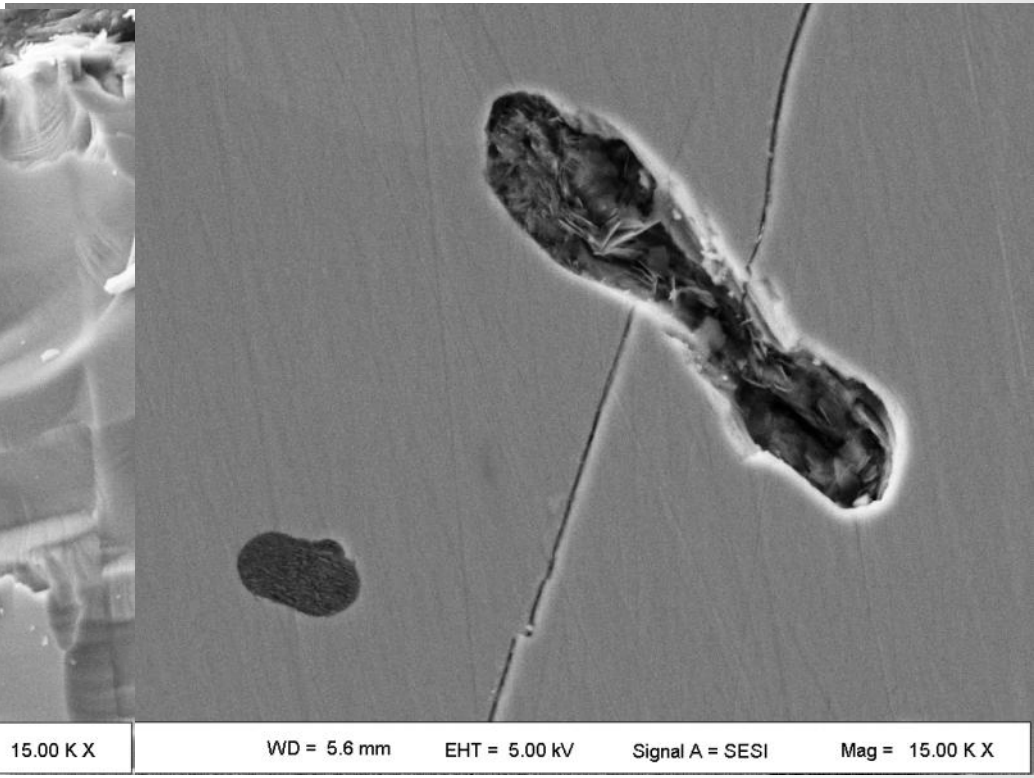




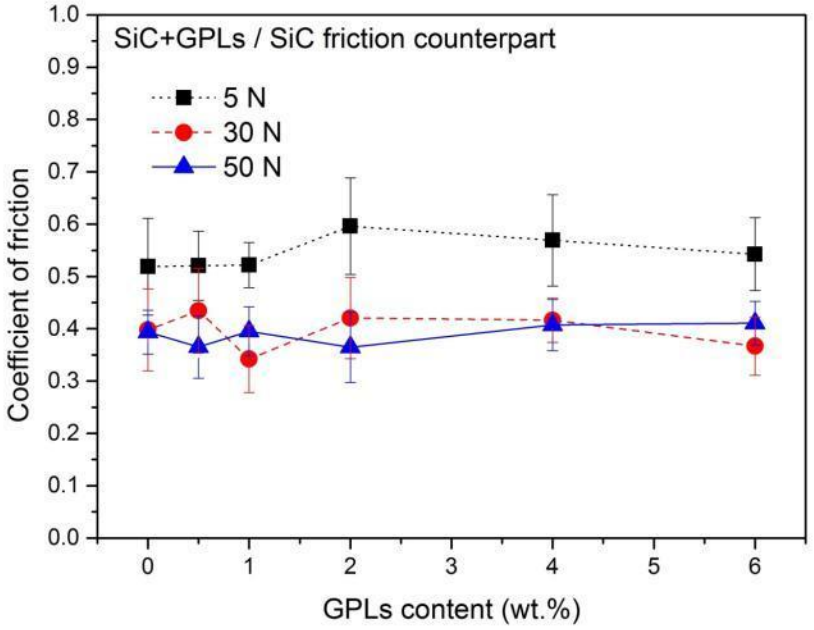


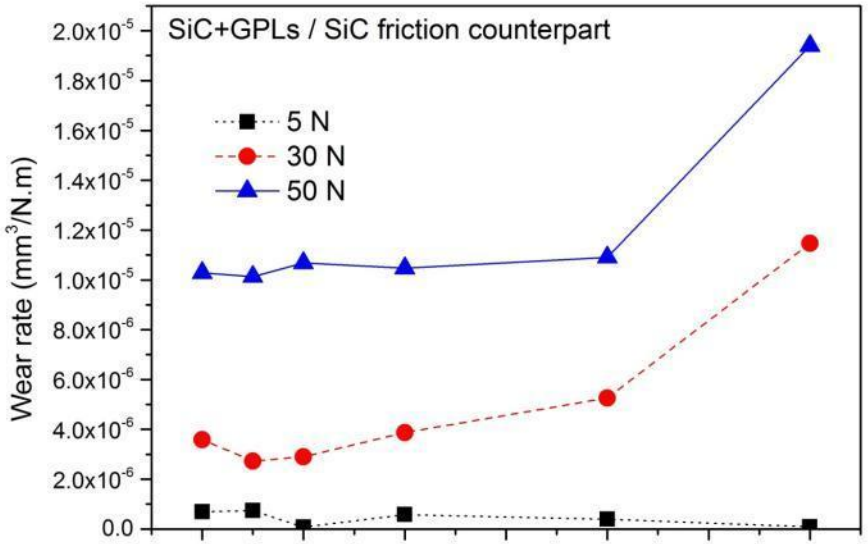
SiC-GPL
fractography – fracture paths

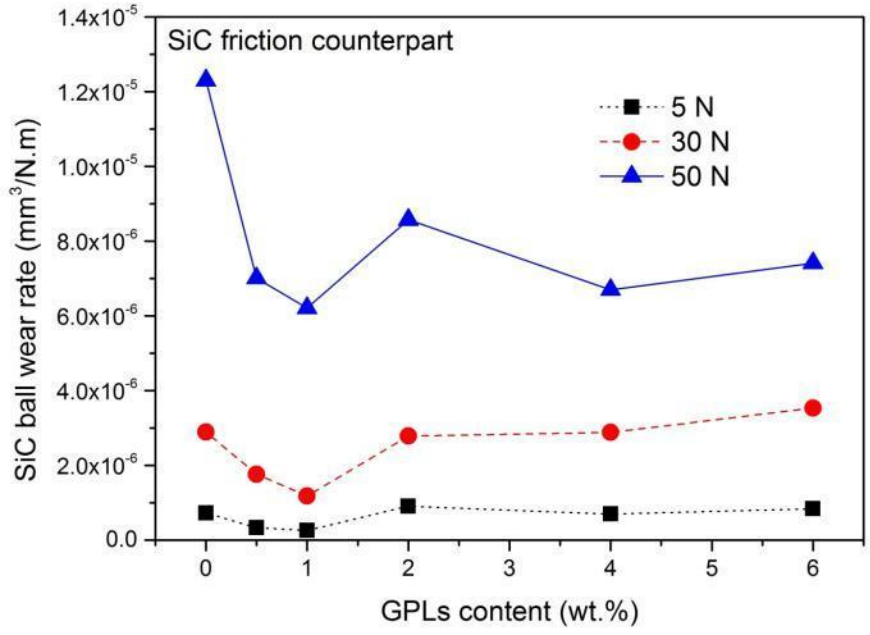




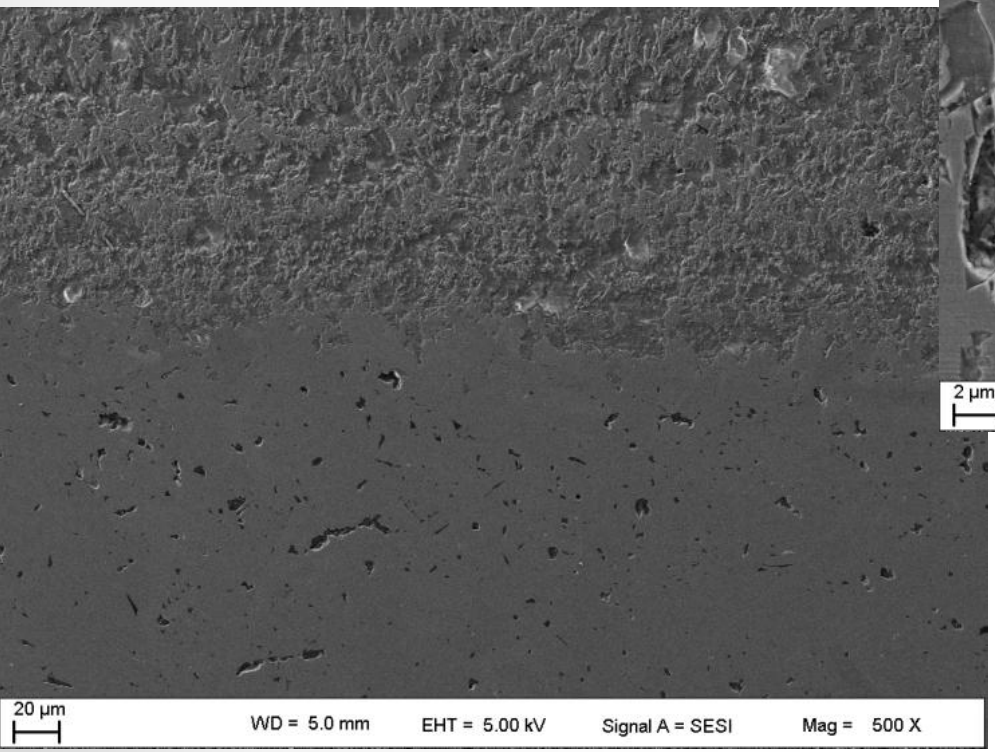
SiC-GPL
tribology: coefficient of friction, wear rates

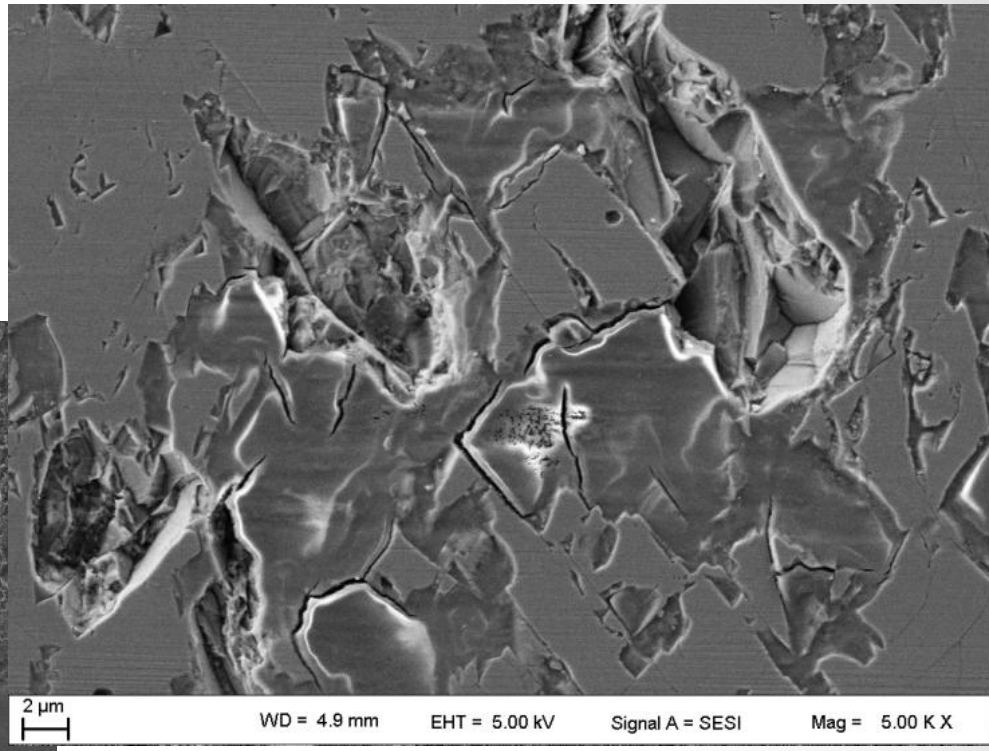




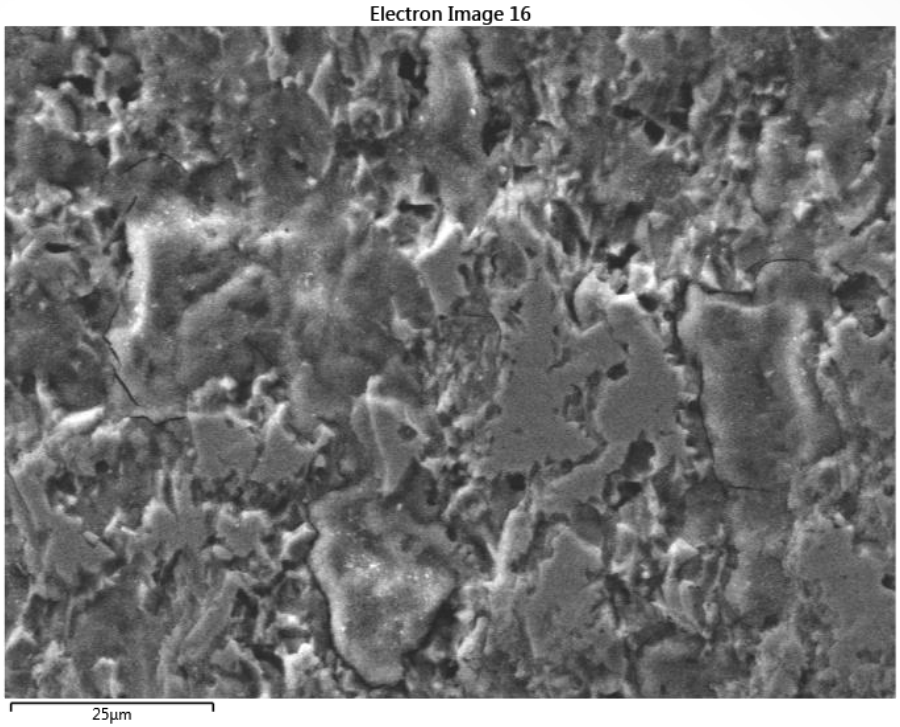


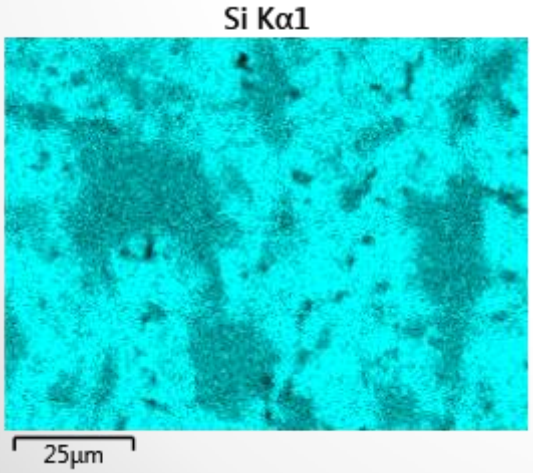
SiC-GPL
tribology: wear character

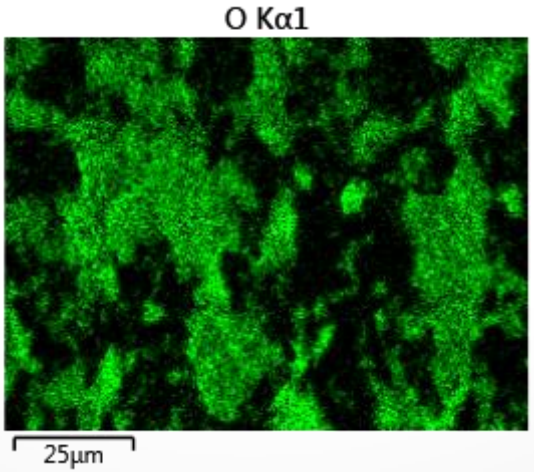


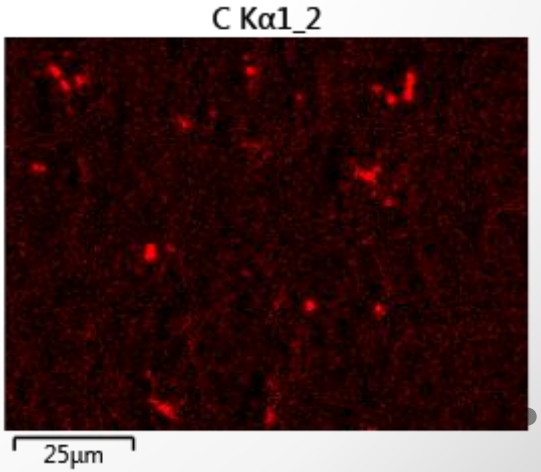


SiC-GPL
tribology: wear character

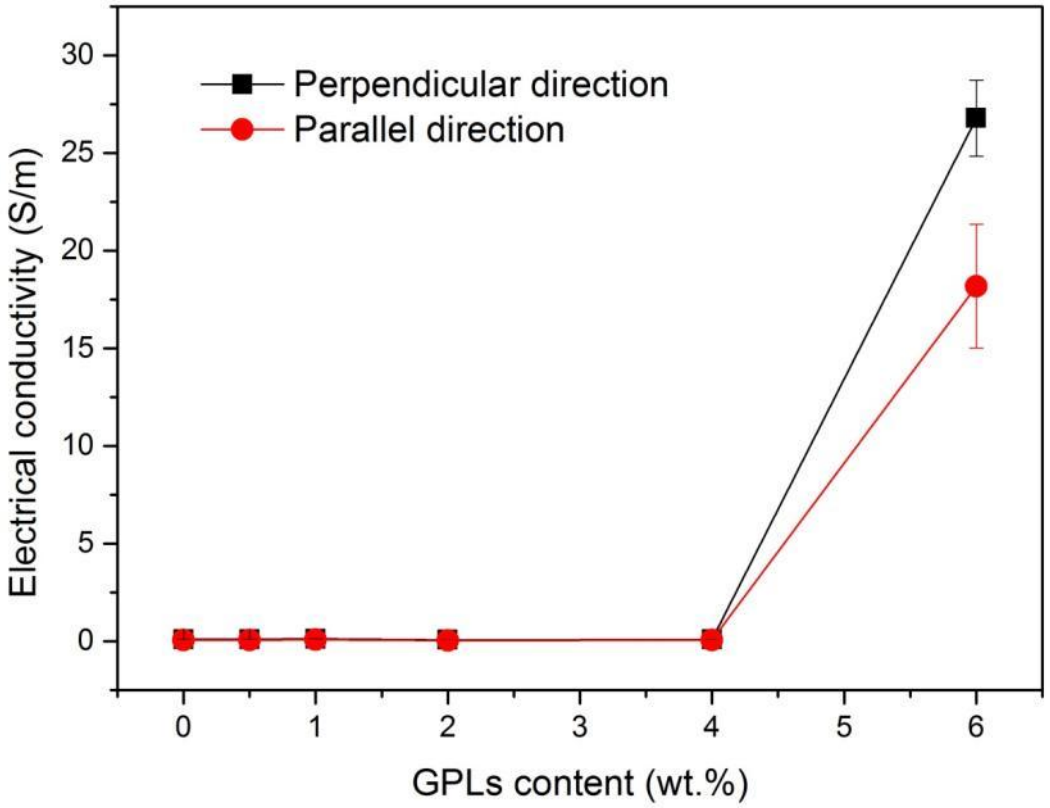








SiC-GPL
Electrical conductivity



SiC-GPL
Conclusions

- 6 materials with GPL prepared
- GPL - preferential orientation, remained in stacks
- Hardness and elasticity decreased
- Toughness and strength improved
- COF 0.4-0.6 – all materials
- Wear rate – 10^{-6}-10^{-5}, mm^3/Nm, higher for high amounts of GPL
- Wear mechanism – cracking, oxidation
- Electrical conductivity insufficient – better distribution of carbon phases required

2. SiC-CNT
Fabrication

1.) Preparation of SiC/CNT powder mixtures by catalytic chemical vapour deposition (CCVD)

Homogenous distribution of solid $Fe(NO_3)_3$ phase from aqueous solution on SiC particles surface

Calcination of $Fe(NO_3)_3$ (750°C/Ar+H_2/60min) Suspension – Freeze granulation

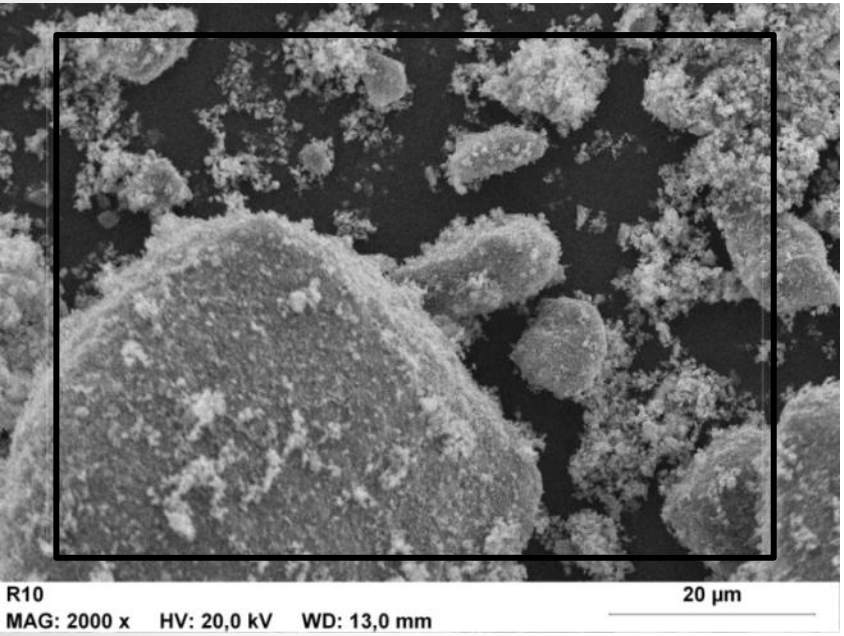
Catalytic Chemical Vapor Deposition (700°C/C_2H_2/Ar/60 min)

2.) Preparation of dense SiC/CNT composite material

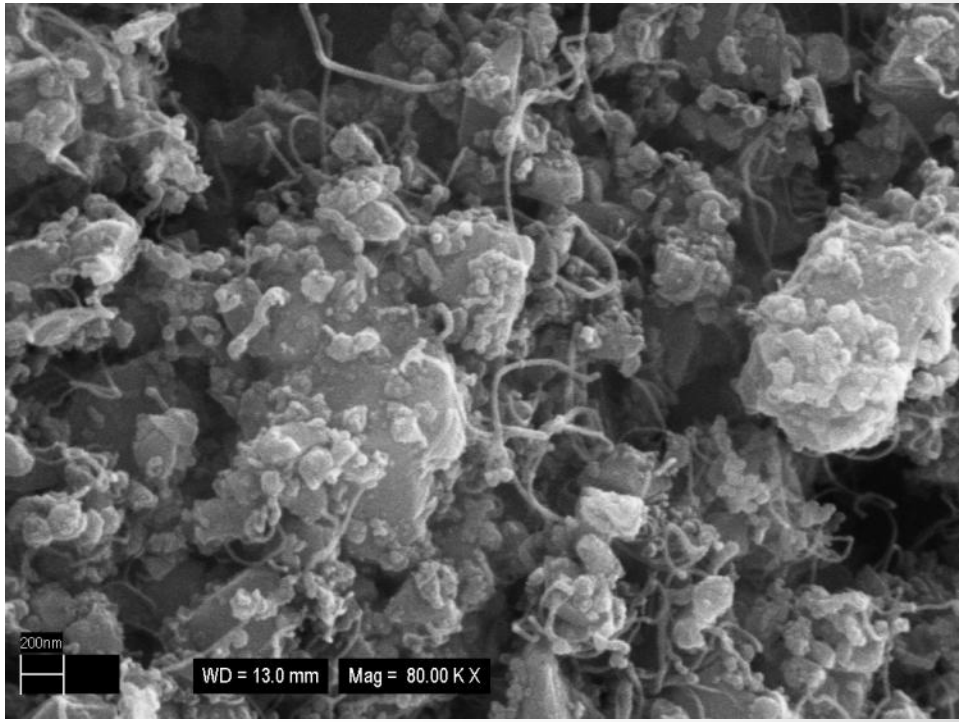
Densification
1850°C / Ar / 60 min / 30 MPa

Fabrication – SiC-CNT

Calcination of $Fe(NO_3)_3$ on SiC particles surface
750°C/1 hour, in Ar + H_2 flow atmosphere



SiC/CNT powder after the chemical deposition.
700° C / 20 min. / Ar + C_2H_2

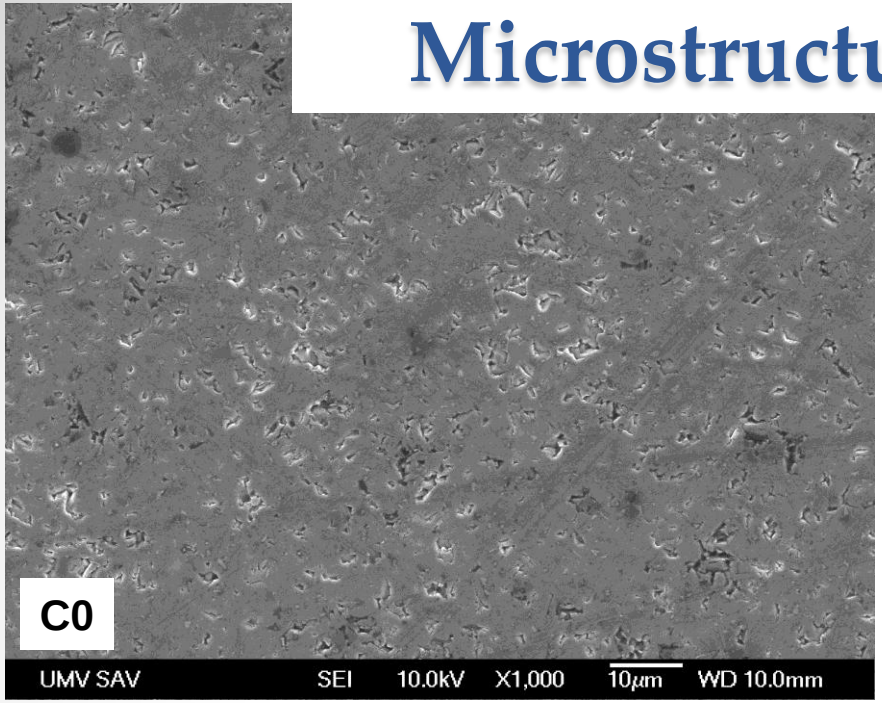


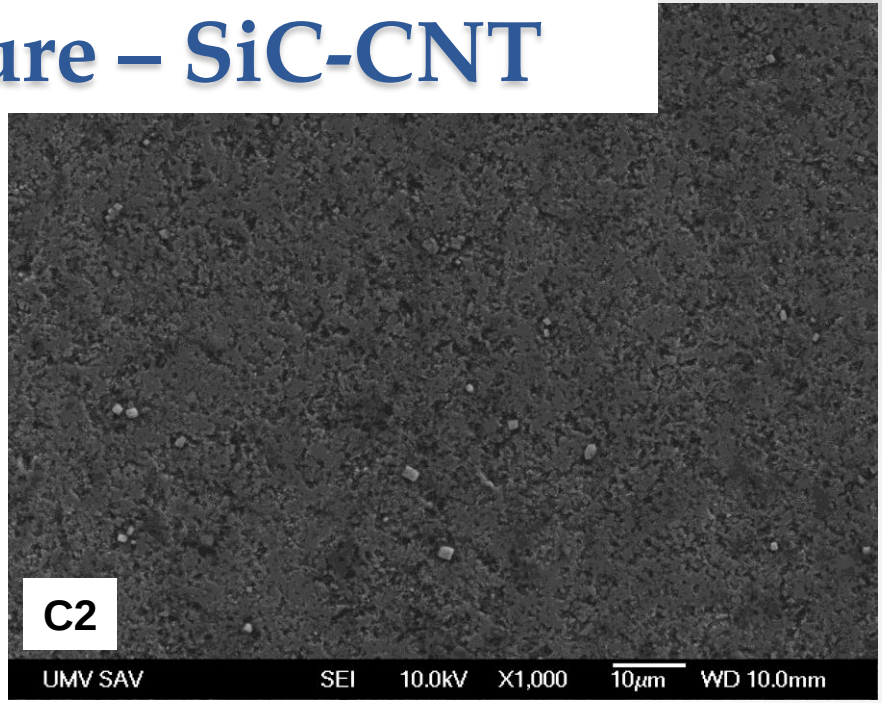
Fabrication – SiC-CNT
resulting materials

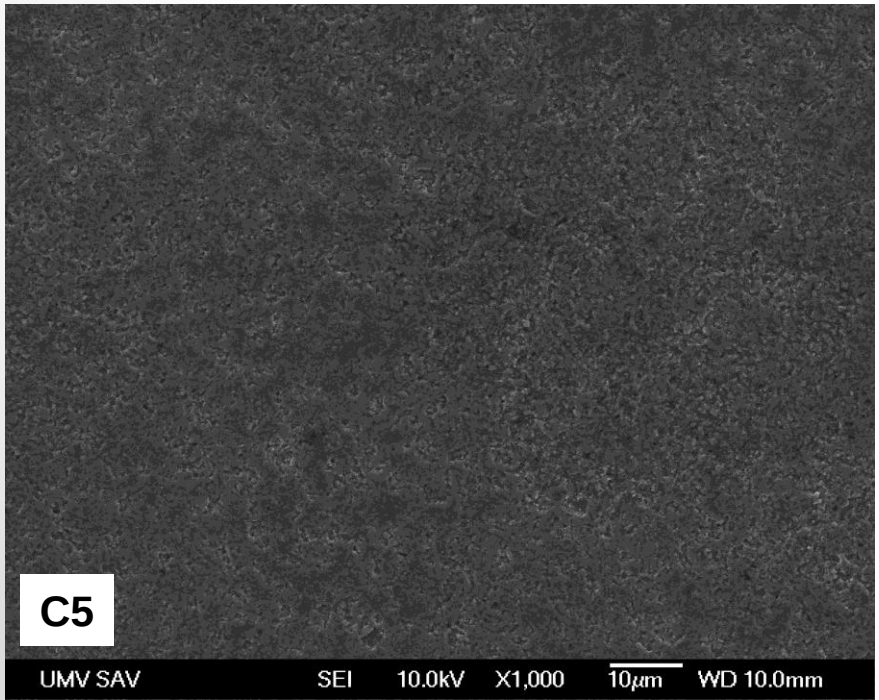
Densification - Hot pressing, 1850°C, Ar, 60 min, 30 MPa

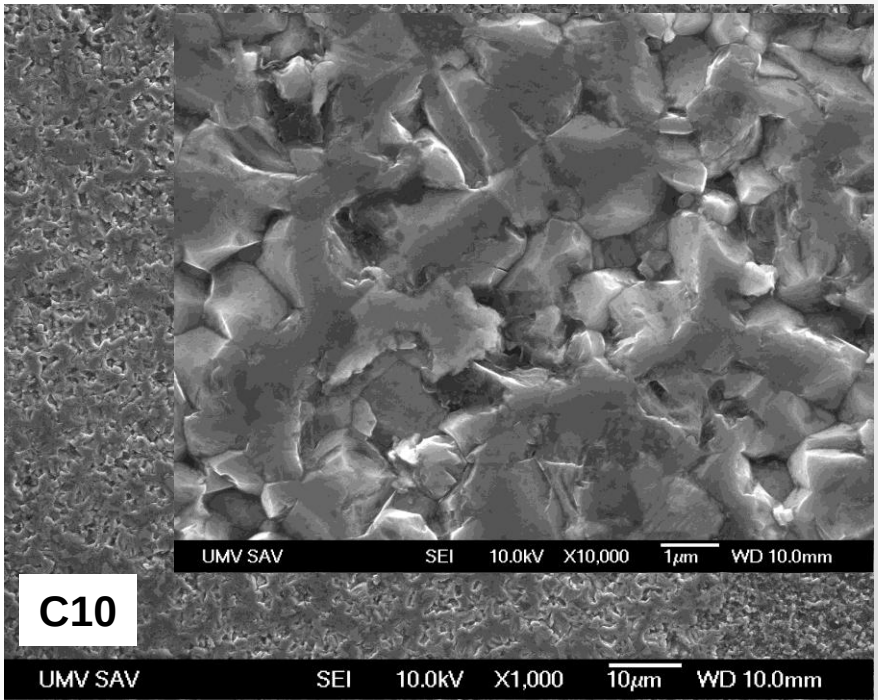
Material	description
C0	reference sample prepared from the starting powder mixture (SiC-2.5wt% Fe catalyst) without CCVD, i.e. no CNTs - to observe the effects of presence of the Fe catalyst on properties but without CNTs.
C2	starting powder mixture with 2.5 wt% Fe catalyst treated by CCVD and CNTs were deposited - SiC-CNT powder pre-cursor fomed.
C5	5 wt% Fe catalyst - increased amount of CNTs
C10	10 wt% Fe catalyst – further increase of CNTs.

Microstructure – SiC-CNT

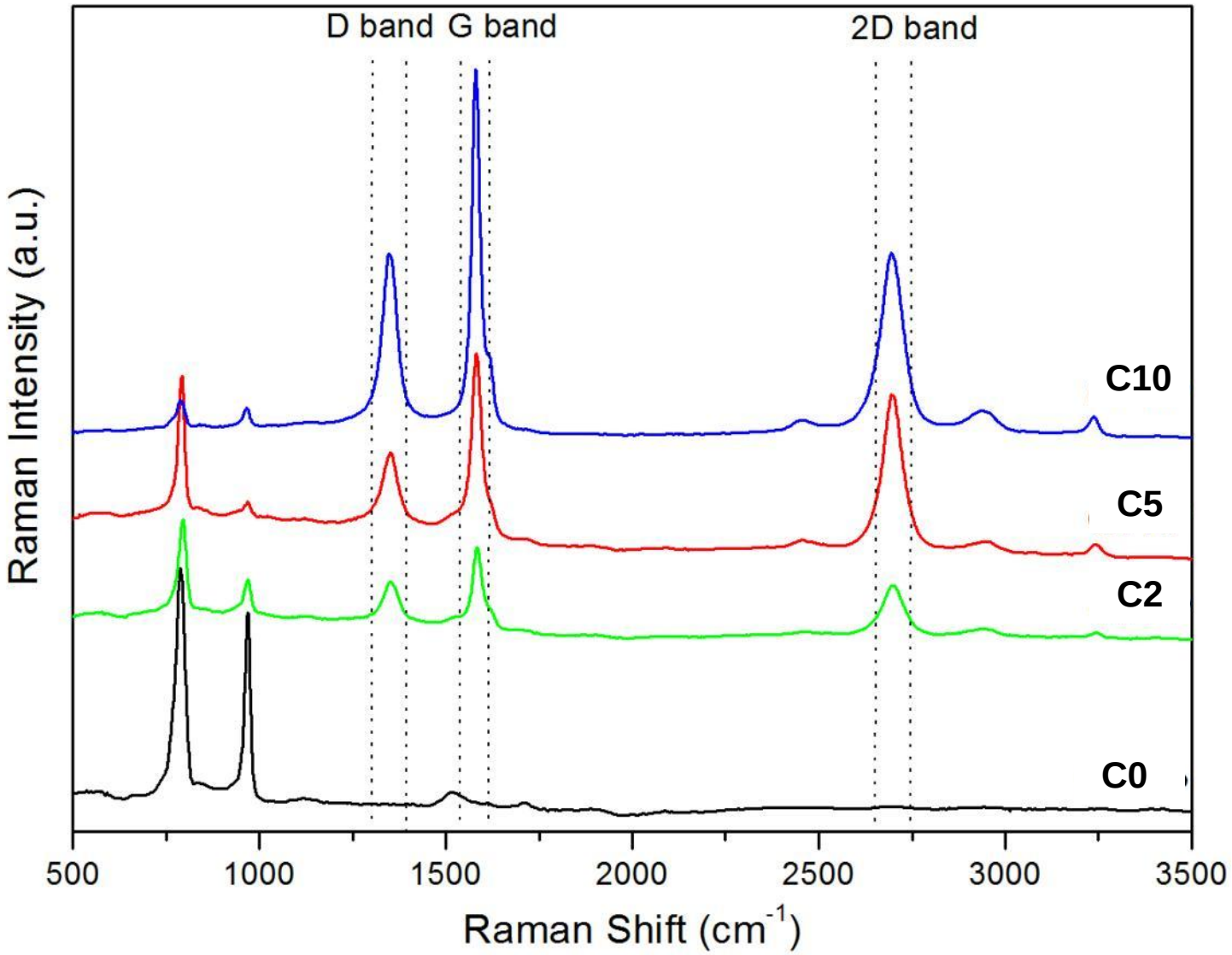








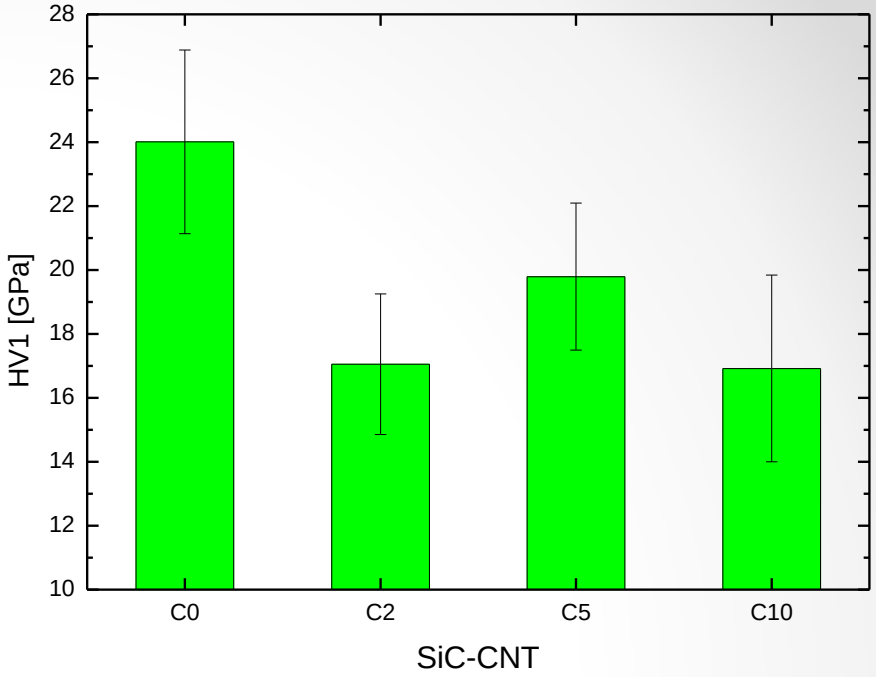
Composition SiC-CNT - Raman

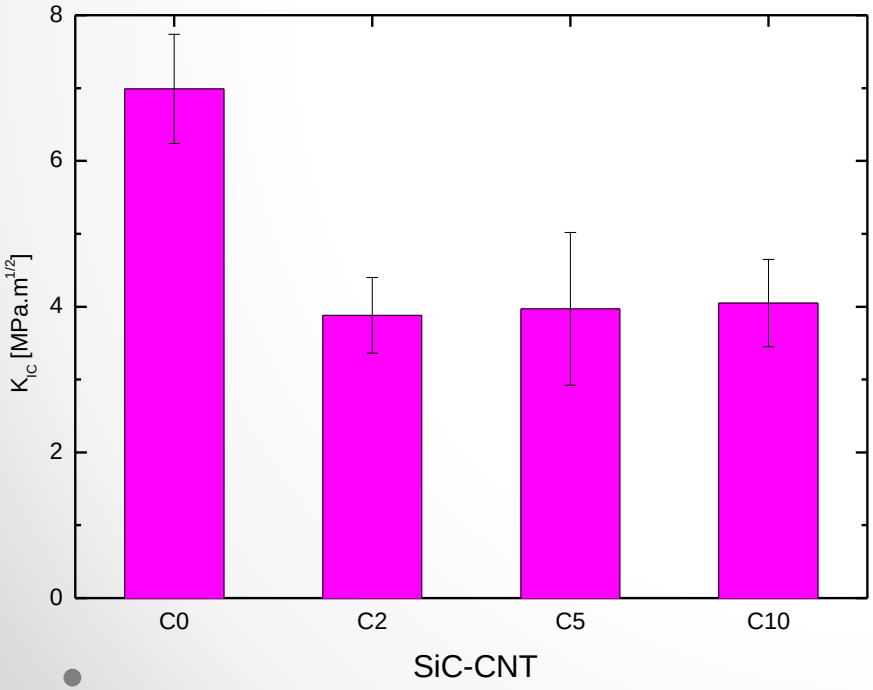


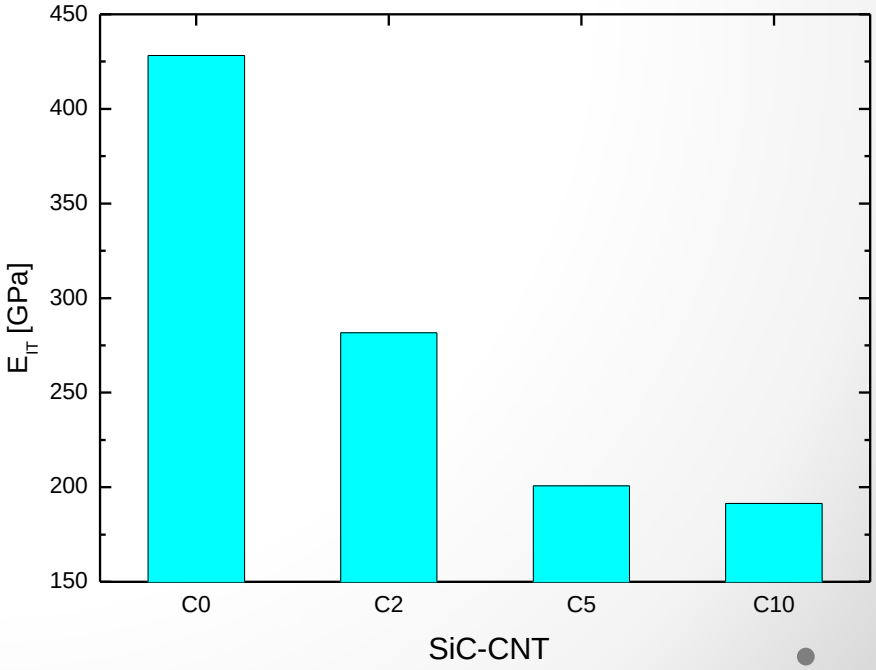
SiC-CNT

Mechanical poperties

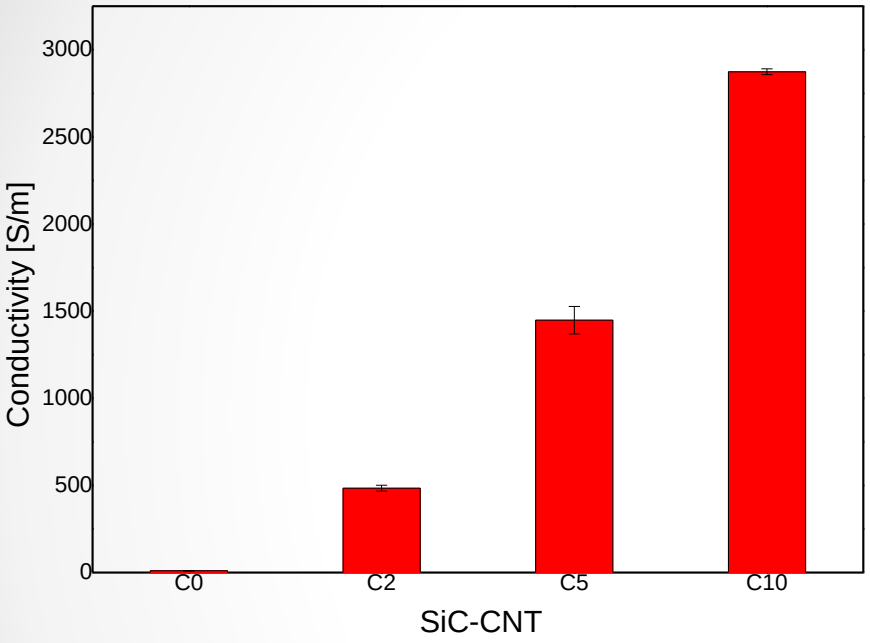
hardness, toughness and modulus

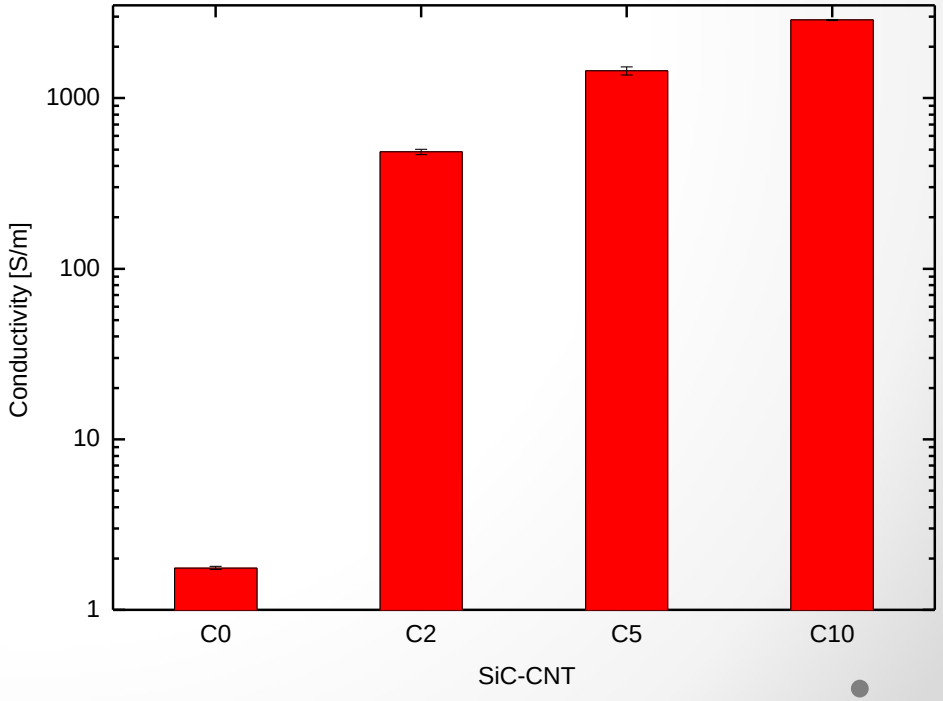




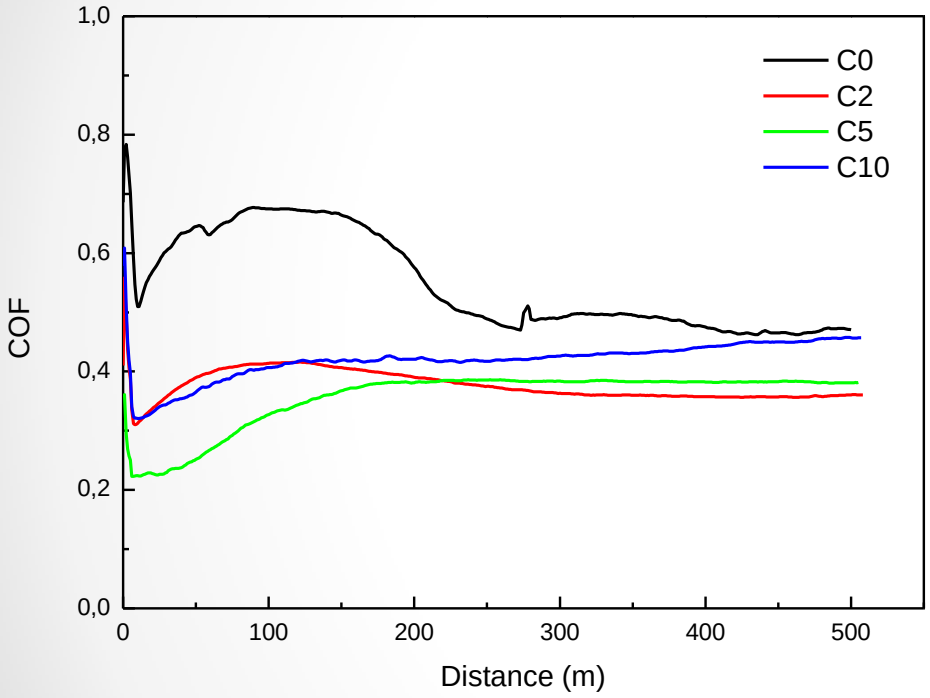


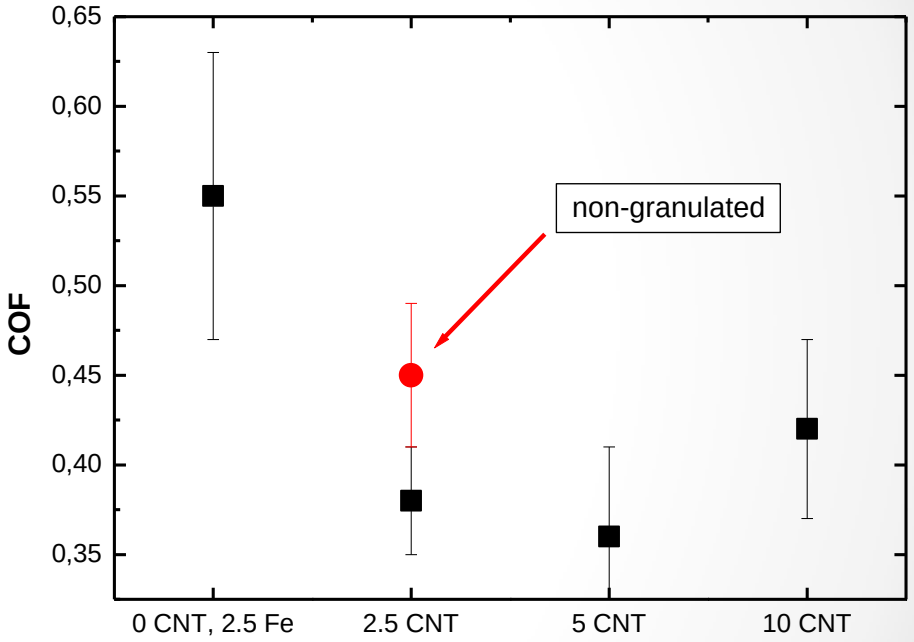
SiC-CNT
Electric conductivity



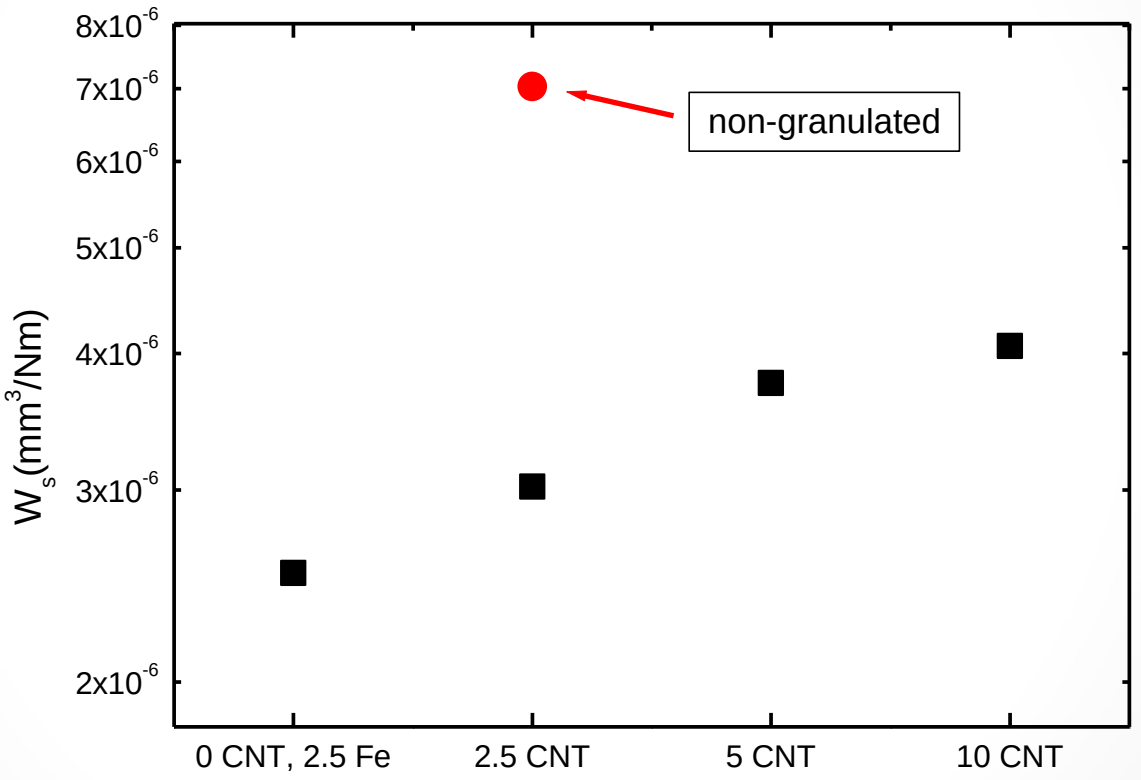


SiC-CNT
Friction

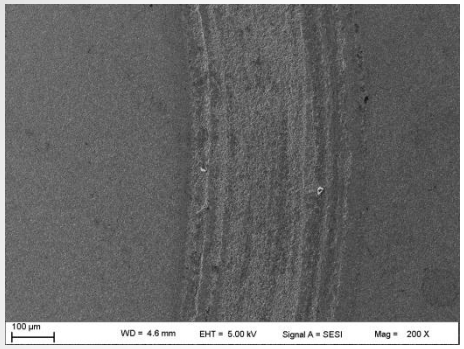
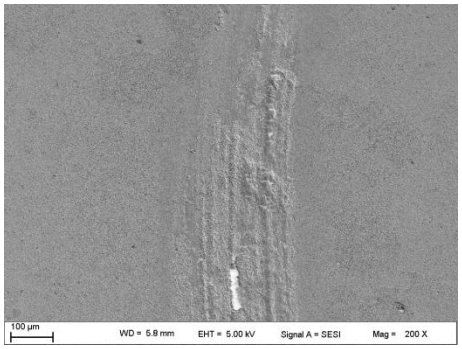
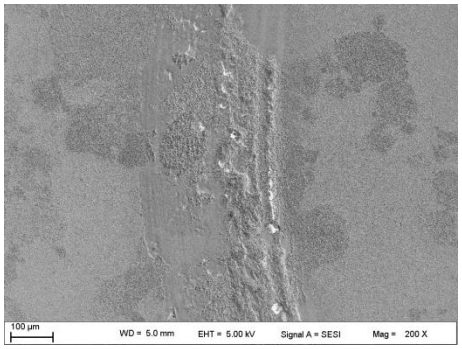
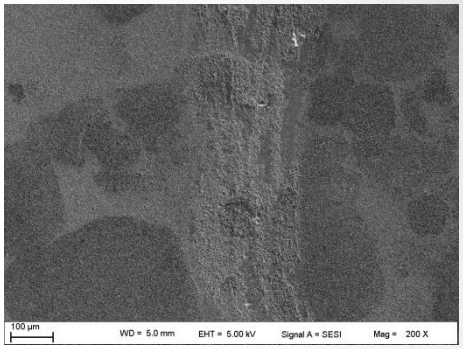
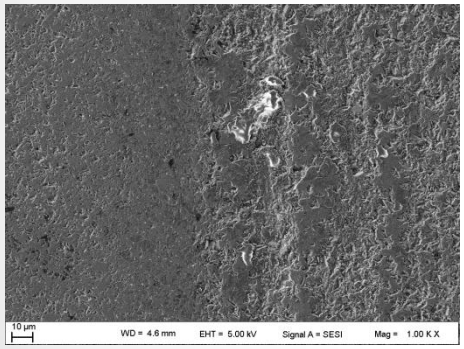
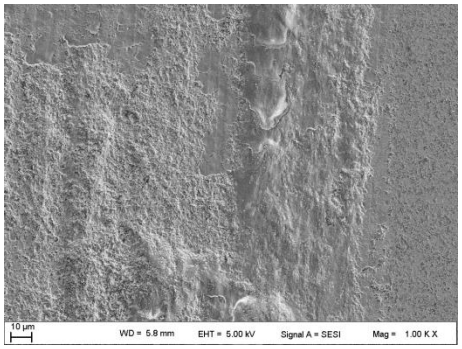
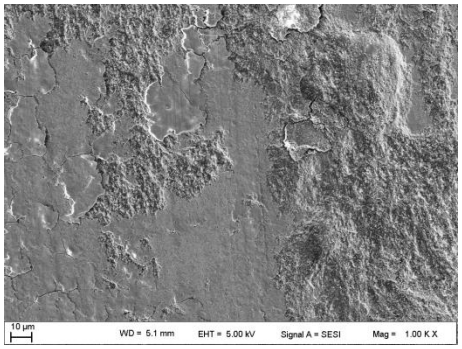
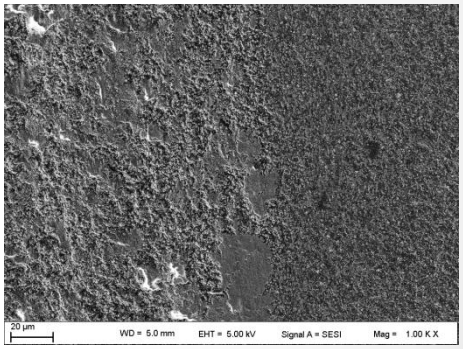
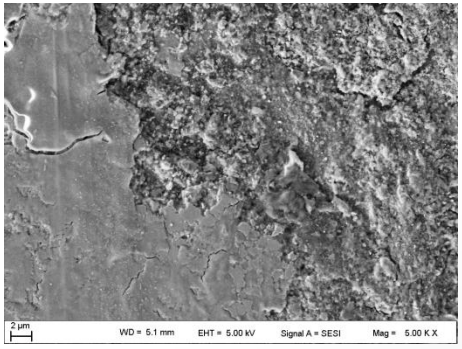
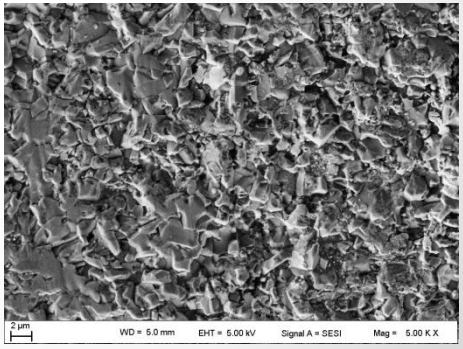




SiC-CNT
wear rate

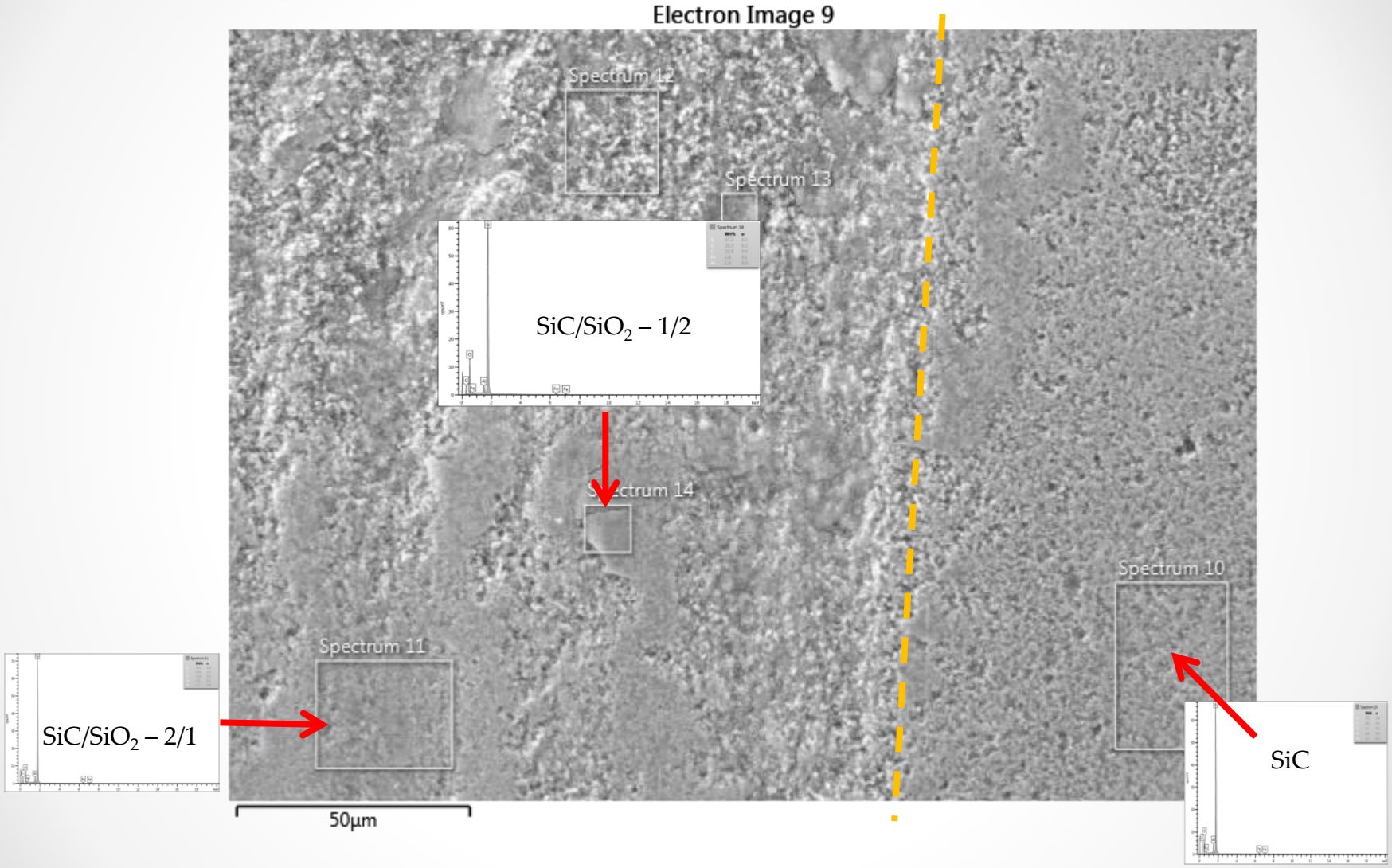


SiC-CNT
wear mechanisms

C0	C2	C5	C10
			
			
			

Abrasion,
Creation oxidic tribolayer
Cracking of oxidic tribolayer
Intergranular cracking for higher CNT

SiC-CNT
wear mechanisms



Conclusions SiC-CNT

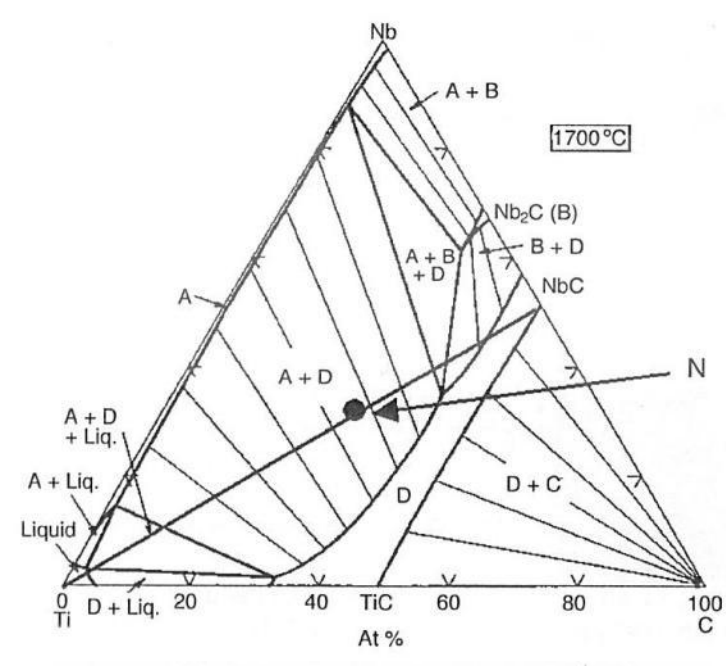
- Three SiC-CNT composites together with reference SiC-(Fe) were prepared by CCVD and HP.
- Microstructure – full densification is a challenge for all materials. Porosity remains.
- Hardness is good considering the porosity. With presence of CNT moderate decrease, from 24 GPa for C0 down to 17-19 GPa.
- Indentation fracture toughness - similarly ~7 MPa.$m^{1/2}$ for C0 down to ~4 MPa.$m^{1/2}$.
- Electric conductivity – increased with amount of CNT and for C5 and C10 exceeded 1000 S/m (1448 S/m and 2873 S/m, resp).
- Friction coefficient lowered from 0,55 down to 0,35-0,45 - almost regardless of CNT amount.
- Wear rate increased almost linearly with CNT, from 2.3x10^{-6} mm^3/Nm for C0 to 4x10^{-6} mm^3/Nm for C10.
- Wear mechanisms – abrasion, oxidation, cracking of oxidic tribolayer.

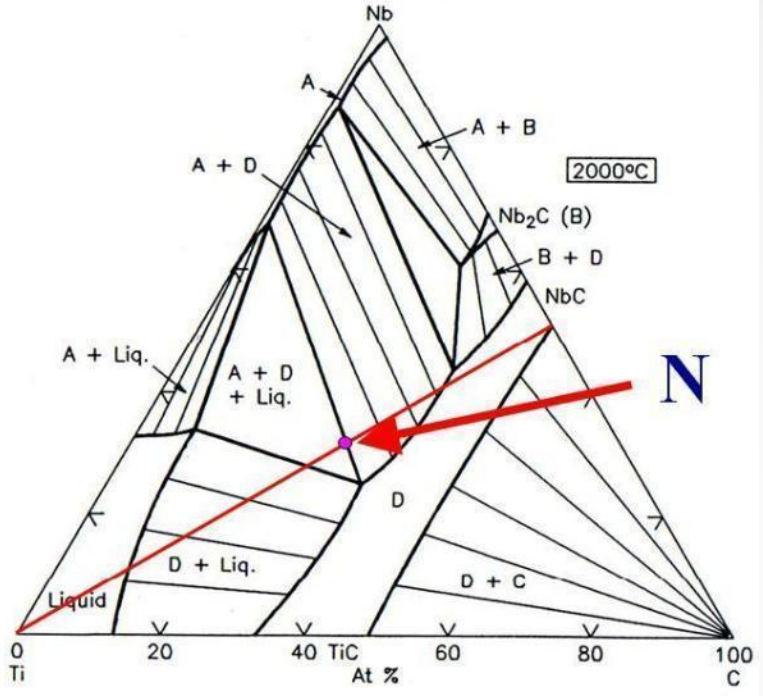
3. SiC-TiNbC

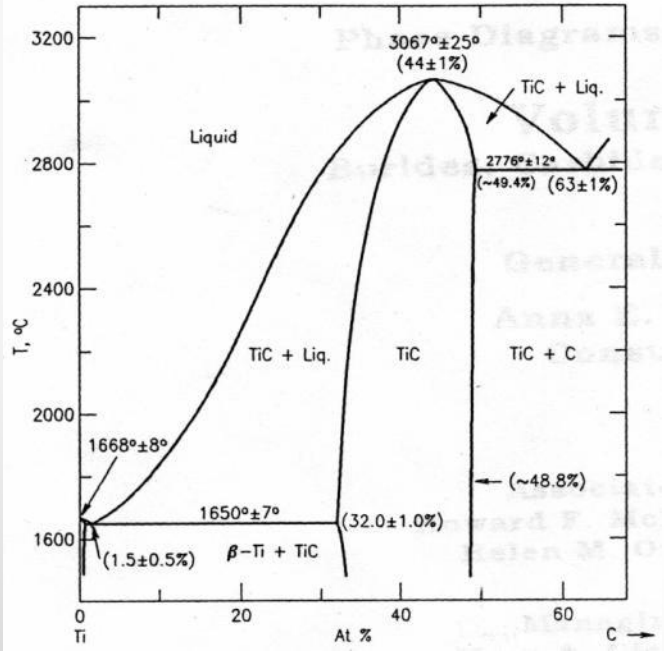
	T_m [°C]	α [10^{-6} K^{-1}]	E [GPa]	HV [GPa]	σ [MPa]	σ_e [S·mm^{-1}]
SiC	2830	4,5	410-450	22-27	550	0,01
TiC	3067	7,4	410-510	28	320	14,7
NbC	3600	6,6	340-580	24	300	13,5

*T*m – melting temperature,
α – thermal expansion coeff.,
E – Youngs modulus,
HV – hardness,
σ – strength,
σ_e [S·mm^{-1}] electric conductivity

SiC + sinter. additives + Ti + NbC



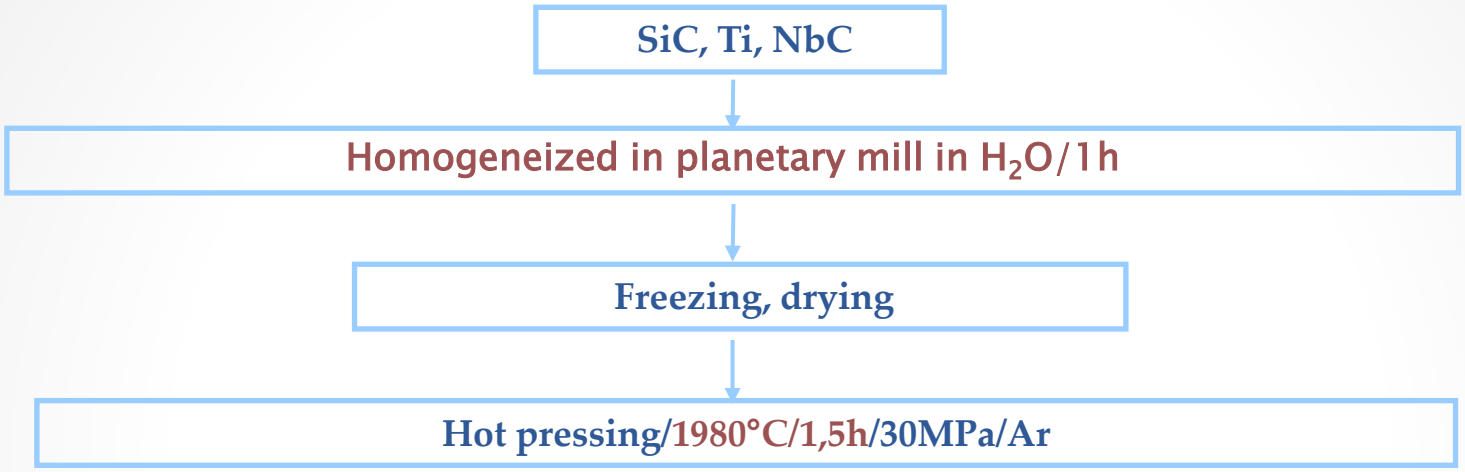




A = $(Nb,Ti)_{(ss)}$
D = $(Ti, Nb)C_{(ss)}$

T_t(Ti) = 1668 °C
T_E(Ti-TiC) = 1650 °C

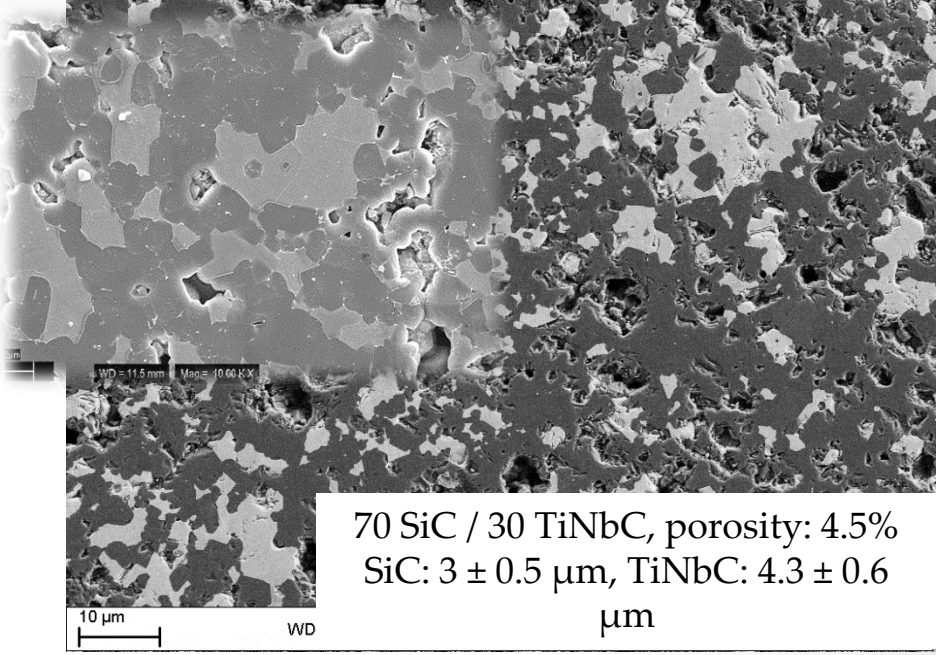
Fabrication – SiC-TiNbC



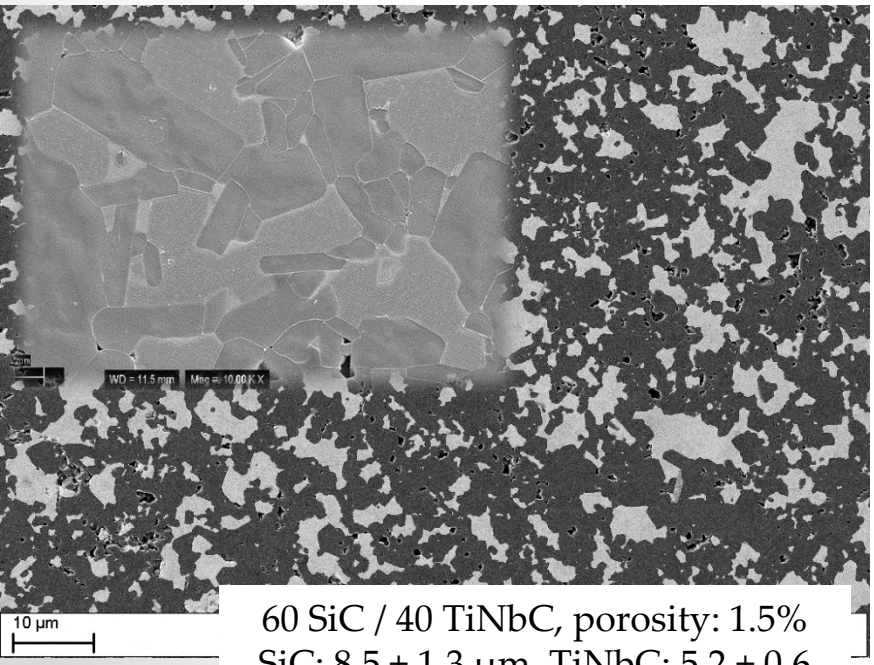
Resulting materials – SiC-TiNbC

	[wt%]		
Sample	SiC	Ti	NbC
SiC30TiNbC	70	10,8	18
SiC40TiNbC	60	14,4	25,6
SiC50TiNbC	50	18	32

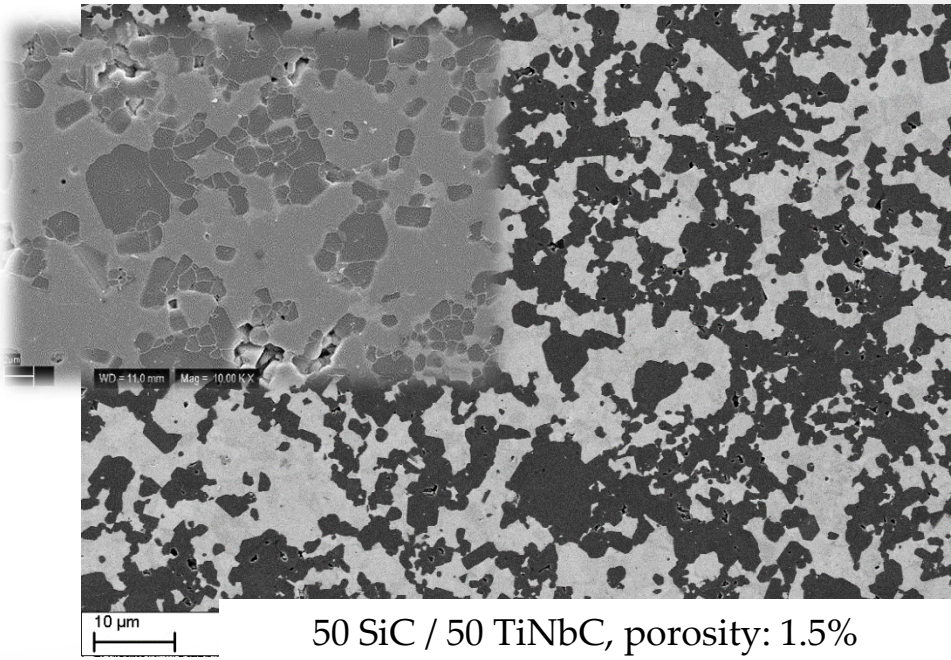
SiC-TiNbC Microstructure



70 SiC / 30 TiNbC, porosity: 4.5%
SiC: 3 ± 0.5 µm, TiNbC: 4.3 ± 0.6 µm

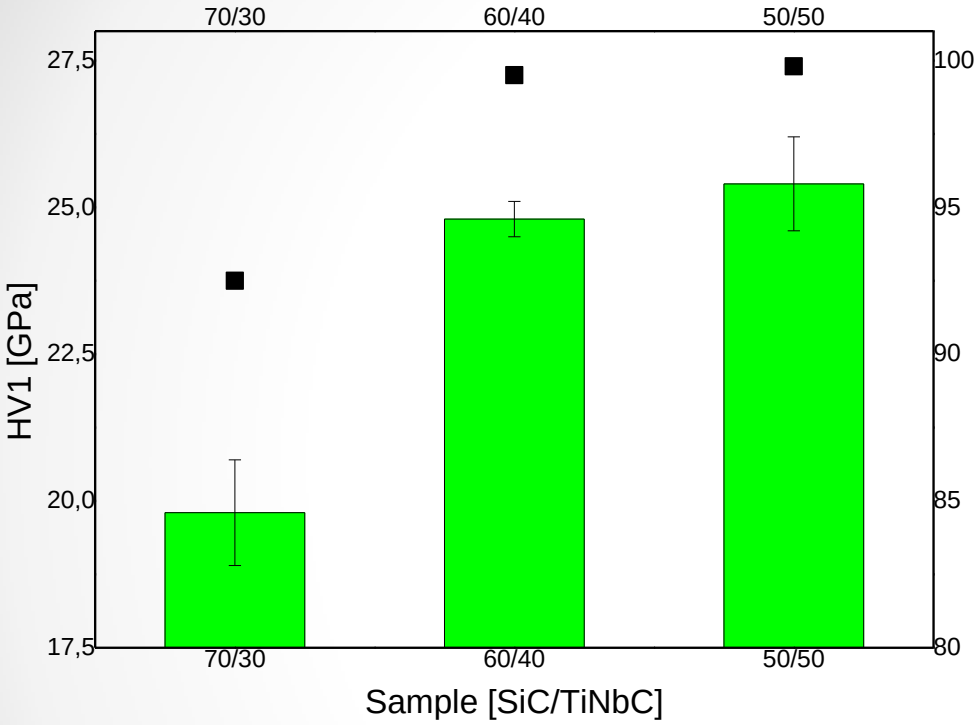


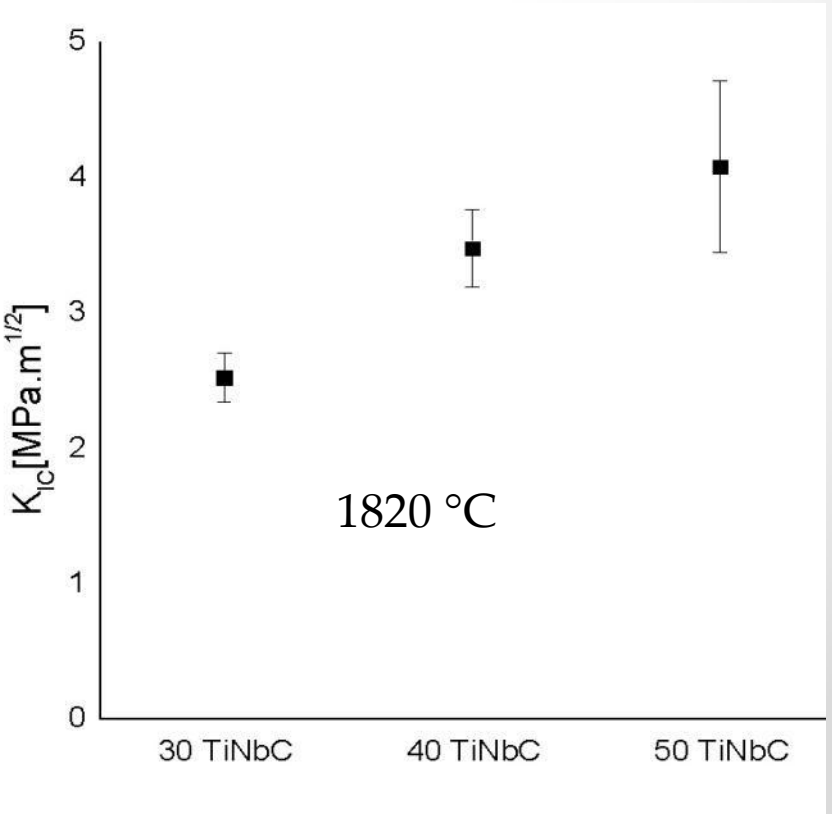
60 SiC / 40 TiNbC, porosity: 1.5%
SiC: 8.5 ± 1.3 µm, TiNbC: 5.2 ± 0.6 µm



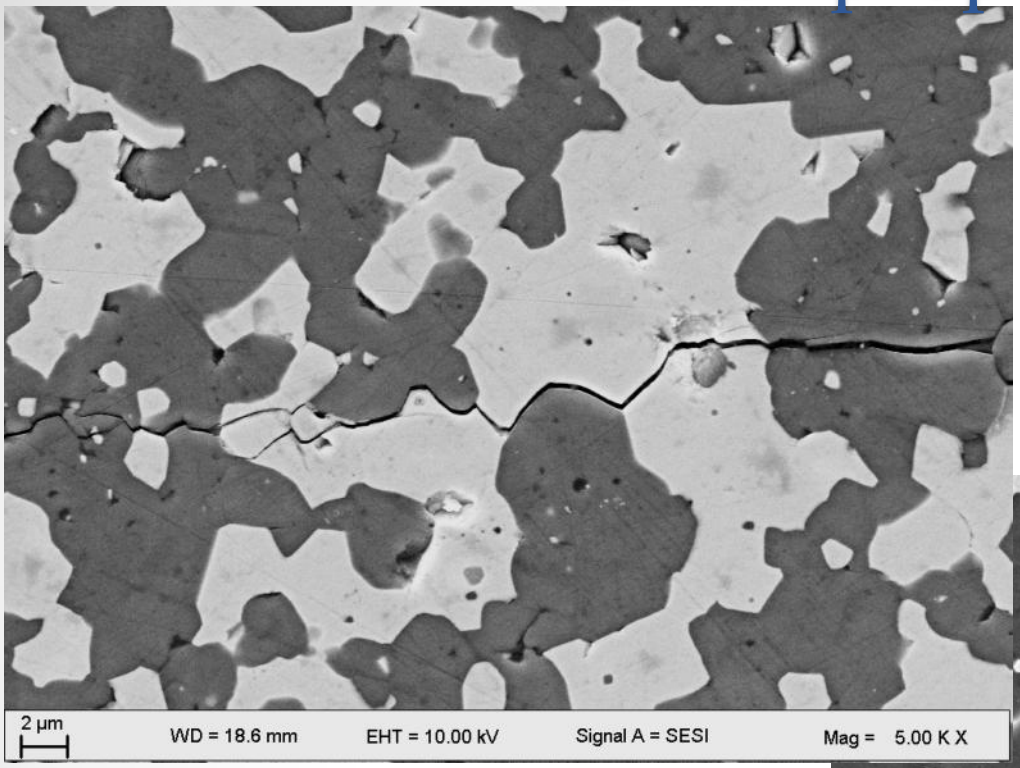
50 SiC / 50 TiNbC, porosity: 1.5%
SiC: 6.2 ± 0.3 µm and 2.3 ± 0.4 µm,
TiNbC: 4.3 ± 0.65 µm

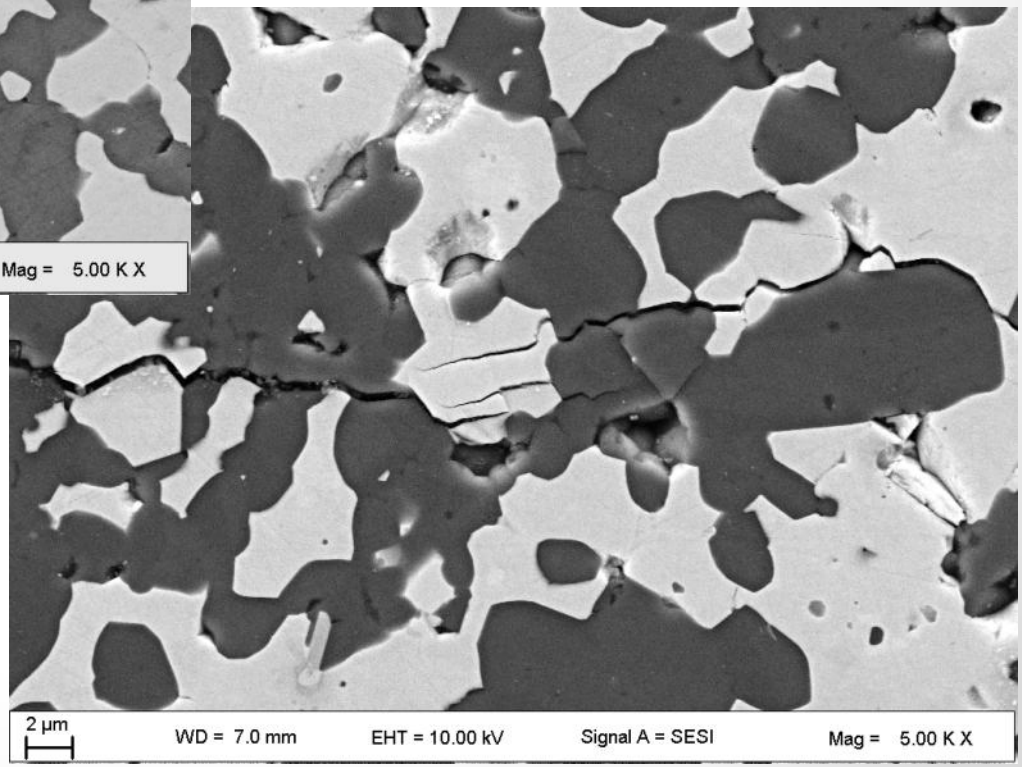
SiC-TiNbC
Hardness and fracture toughness



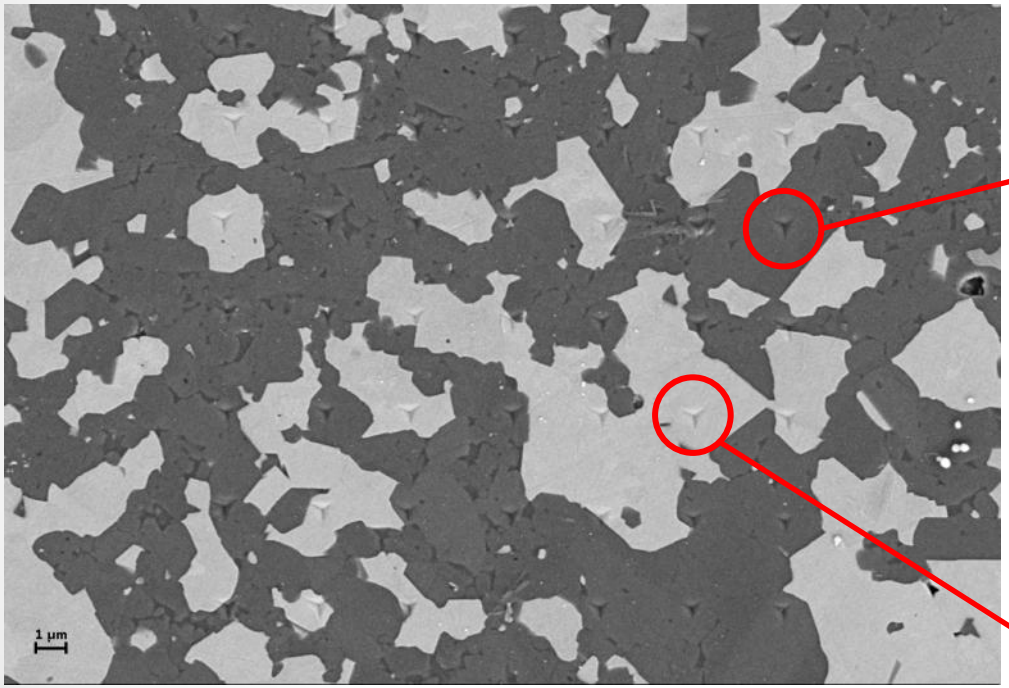


SiC-TiNbC
Crack propagation

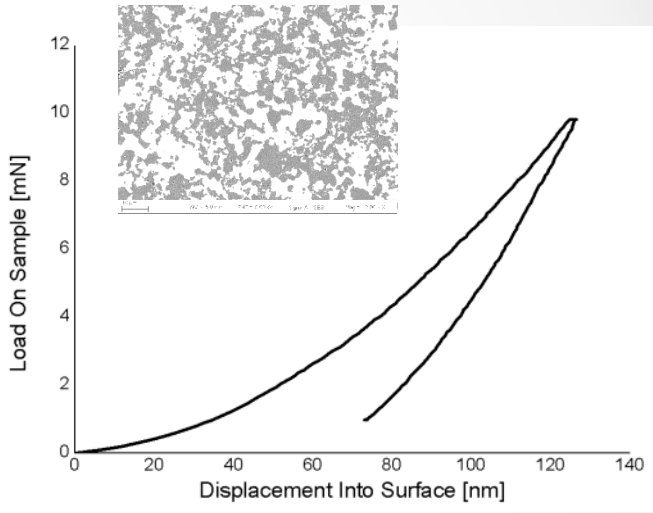


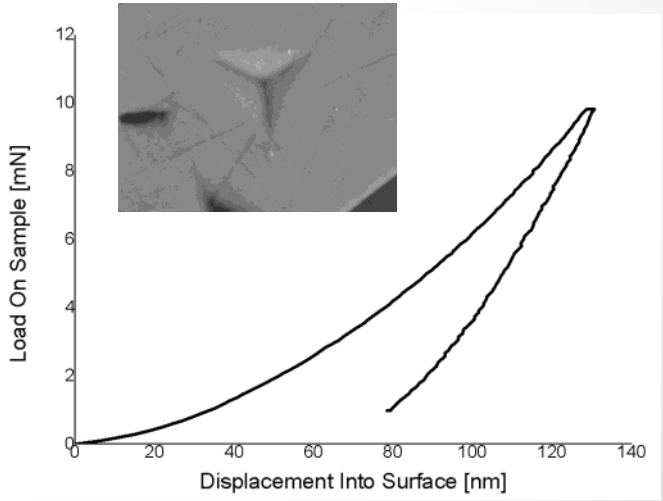


SiC-TiNbC
nanoindentation

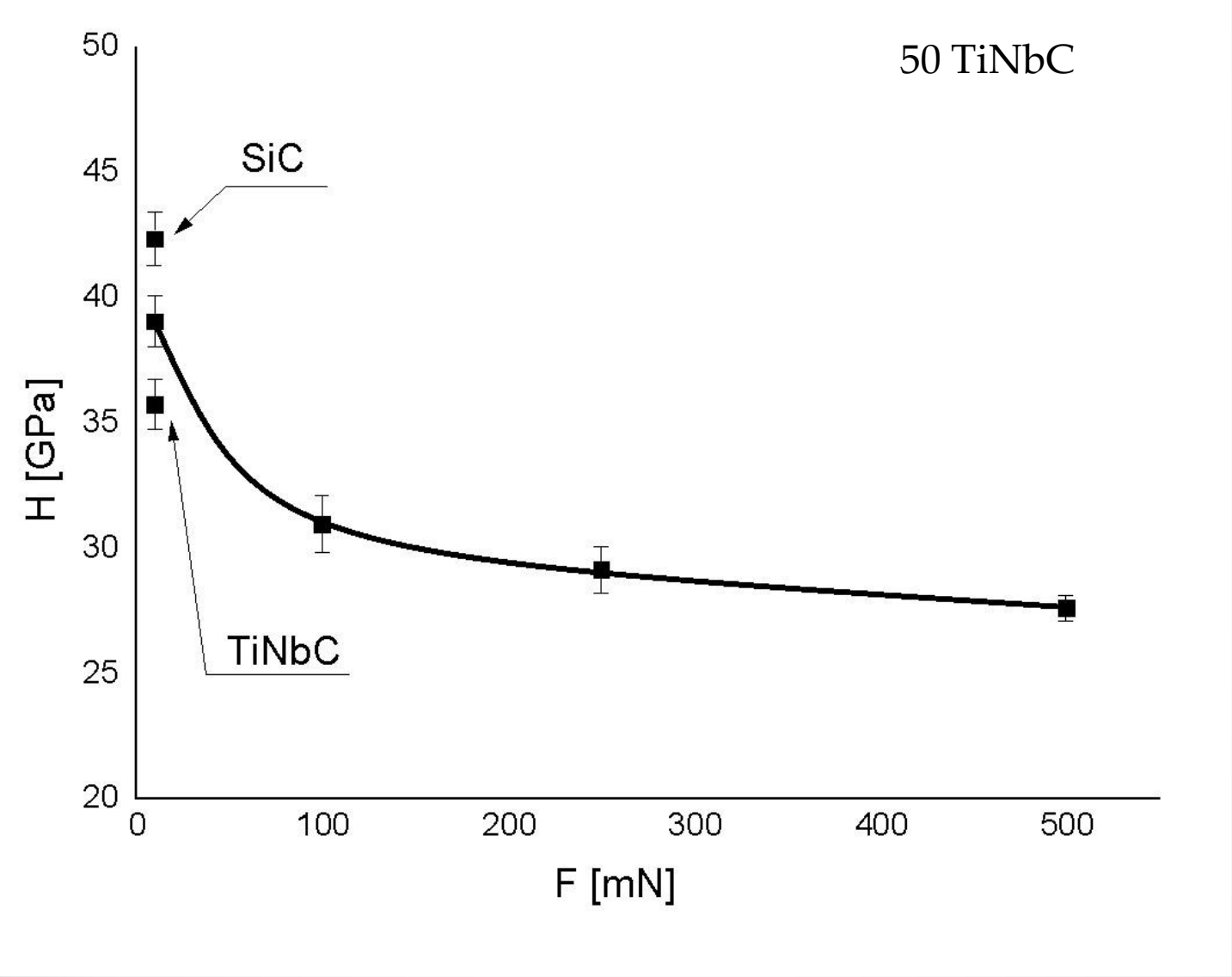


50 TiNbC

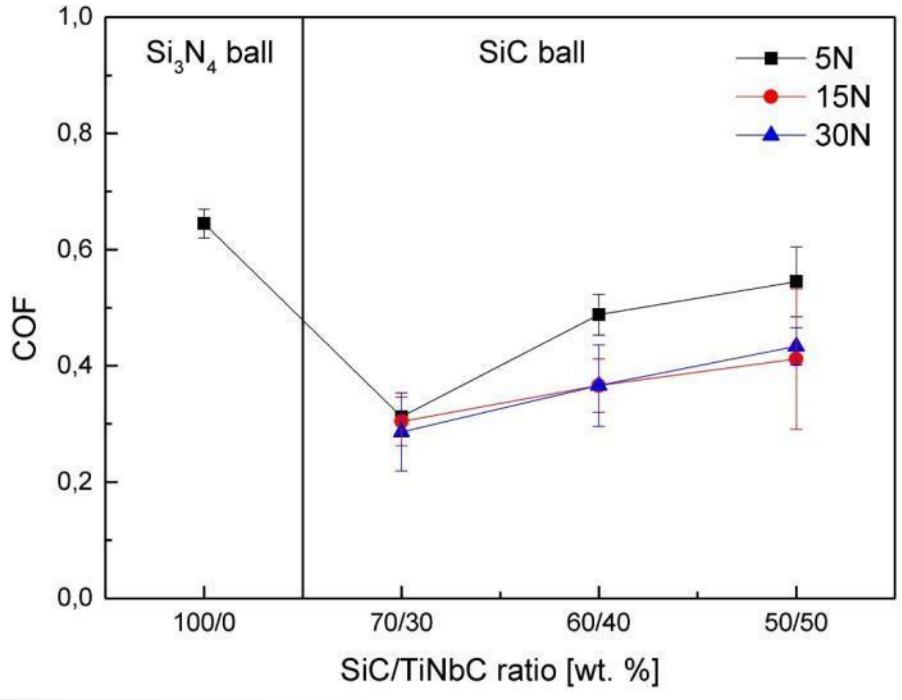


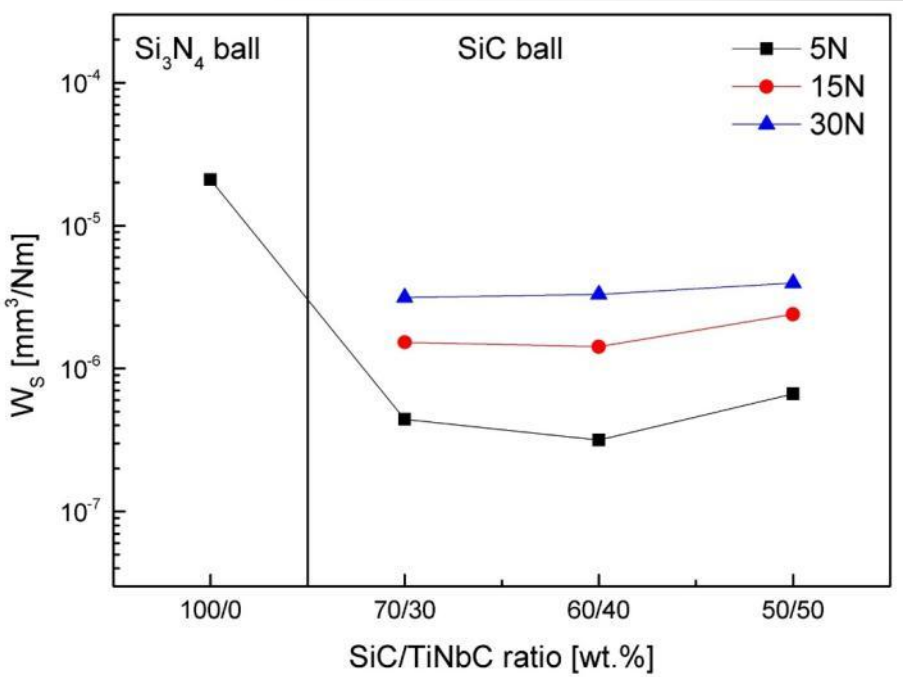


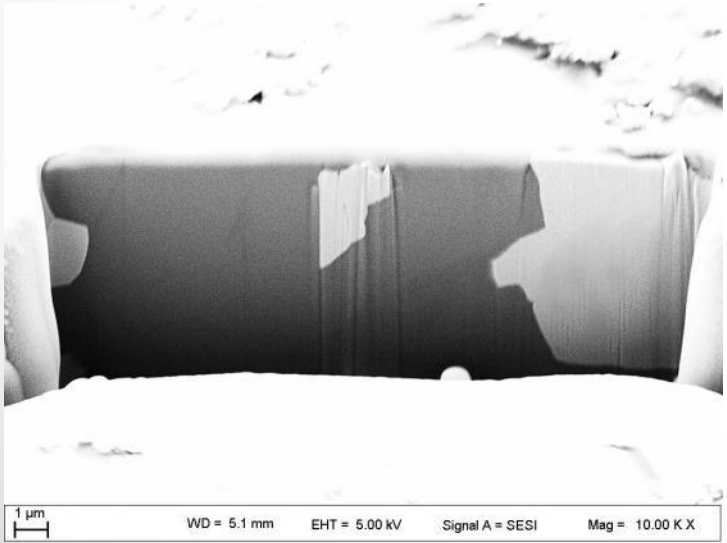
SiC-TiNbC
nanoindentation

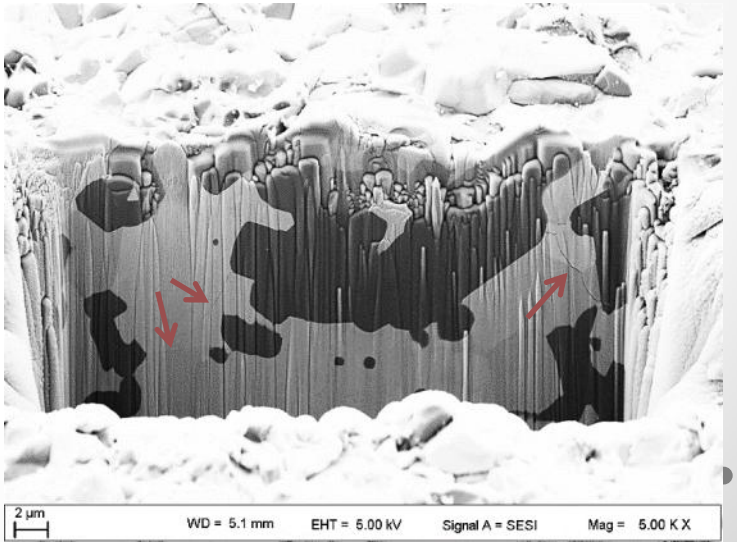


SiC-TiNbC
friction and wear

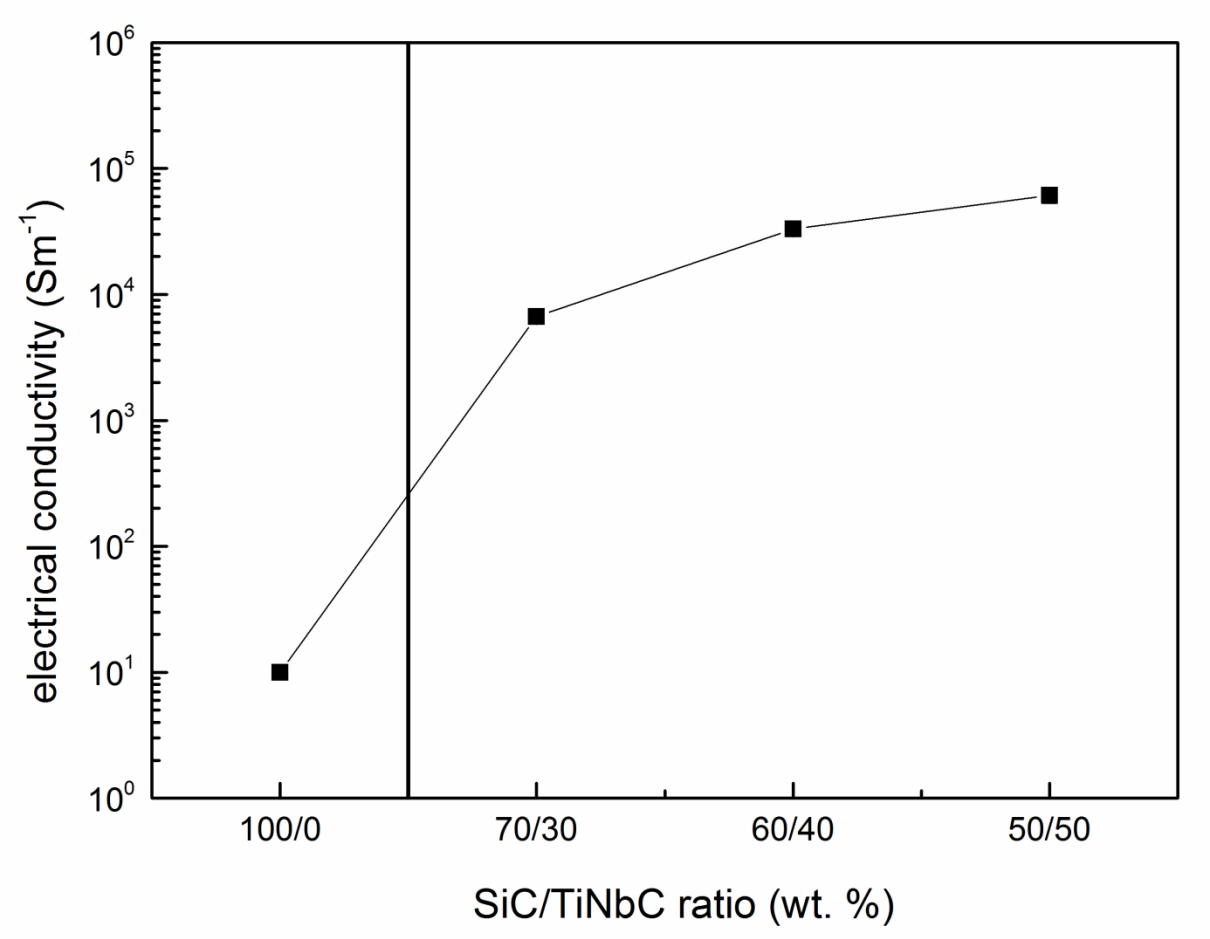








SiC-TiNbC
Electric conductivity



Characterization
Machining – cutting (SiC/TiNbC)

WATER JET (water + abrasive):

P=360MPa
mA=400 g/min mass flow of abrasive
z= 1 mm nozzle distance
d= 0,13/0,35
0,33/0,9 mm
abrasive: Australian garnet 80 MESH

DIAMOND CUTTING WHEEL:

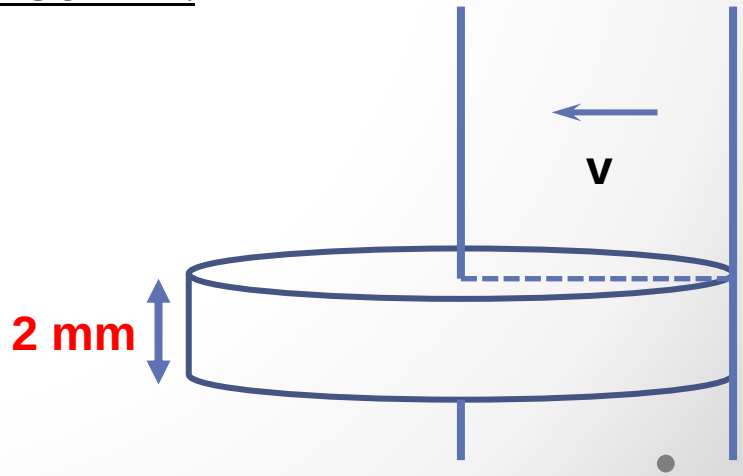
4000 rpm
Water cooling

LASER:

Continuous, power 300W
Focusing 0.2 mm below the specimen surface
Cu base as a heat sink
On air

ELECTRIC SPARK:

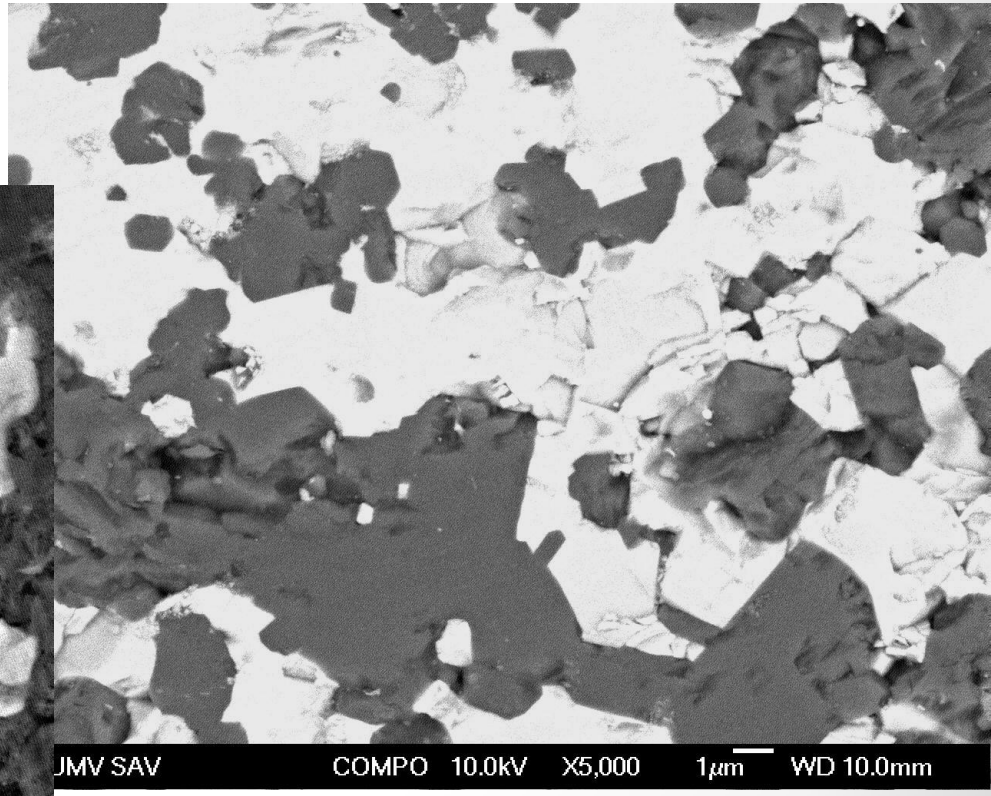
I=0,4 A
U=60V



SiC-TiNbC cutting

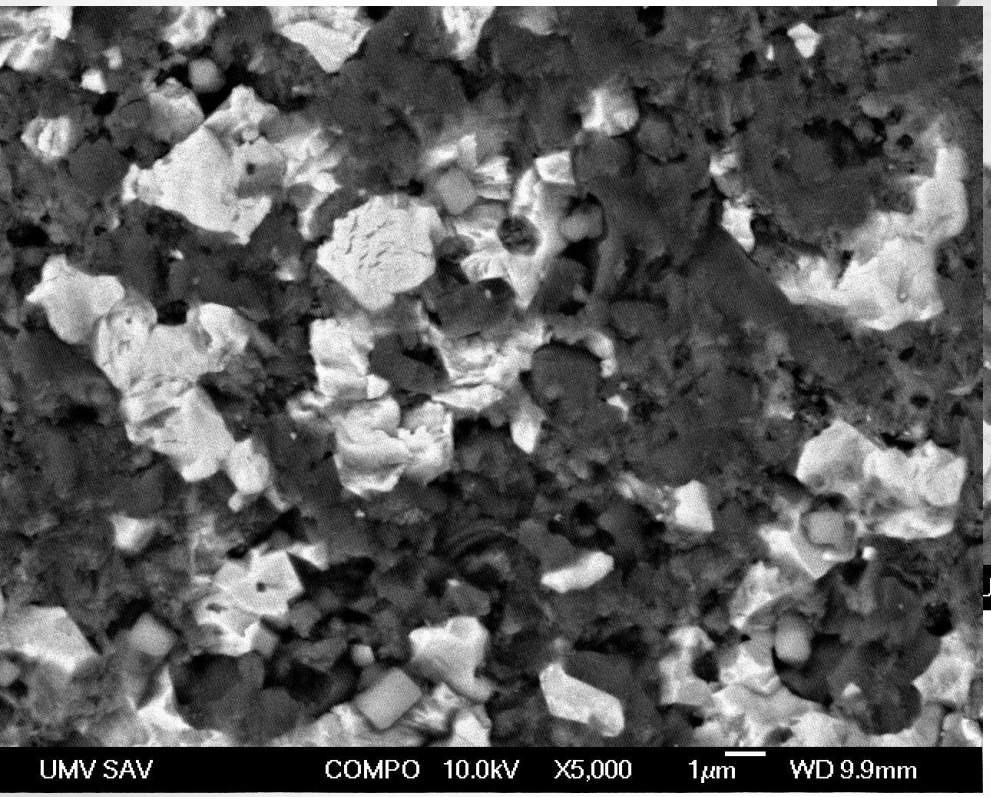
<u>DIAMOND CUTTING WHEEL</u>:

v = 6 mm/min (100um/s)
Smooth cut



<u>WATER JET</u> (water + abrasive):

v = 3 mm/min
Extensive microcracking, erosion, grain breakage

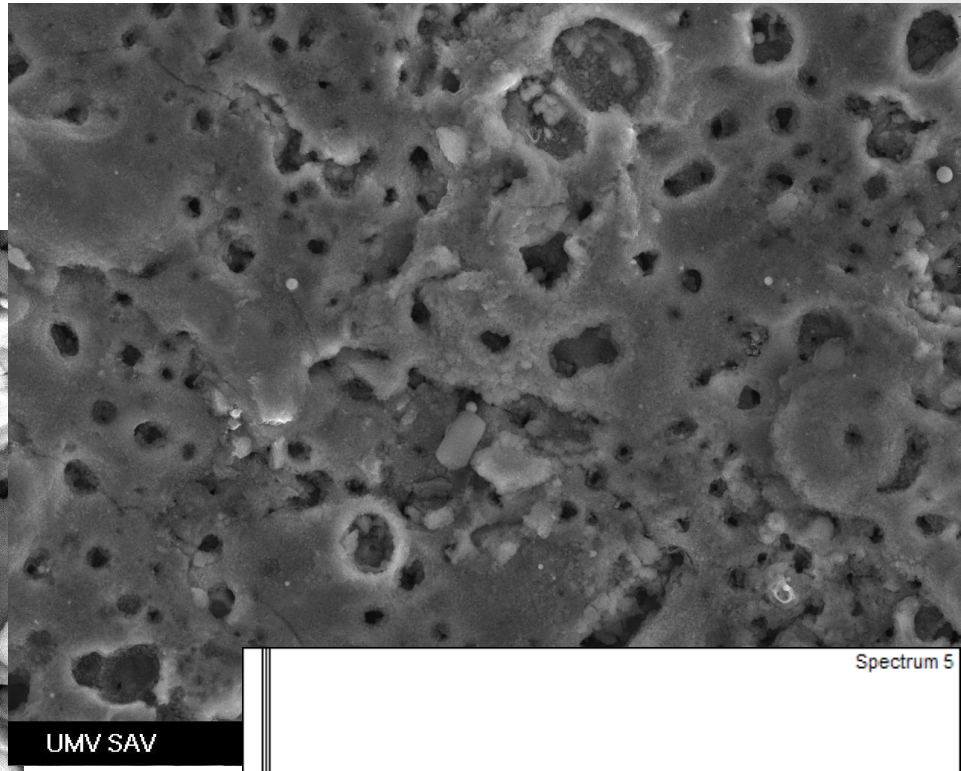


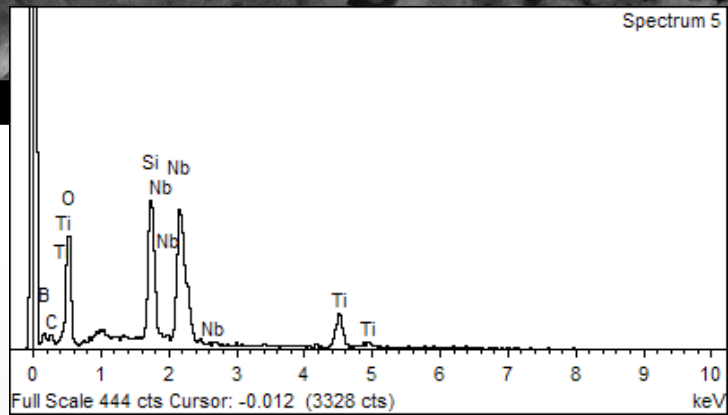
SiC-TiNbC cutting

EDM:

v = 1,39mm/min

Intense oxidation of cut and surfaces around the wire

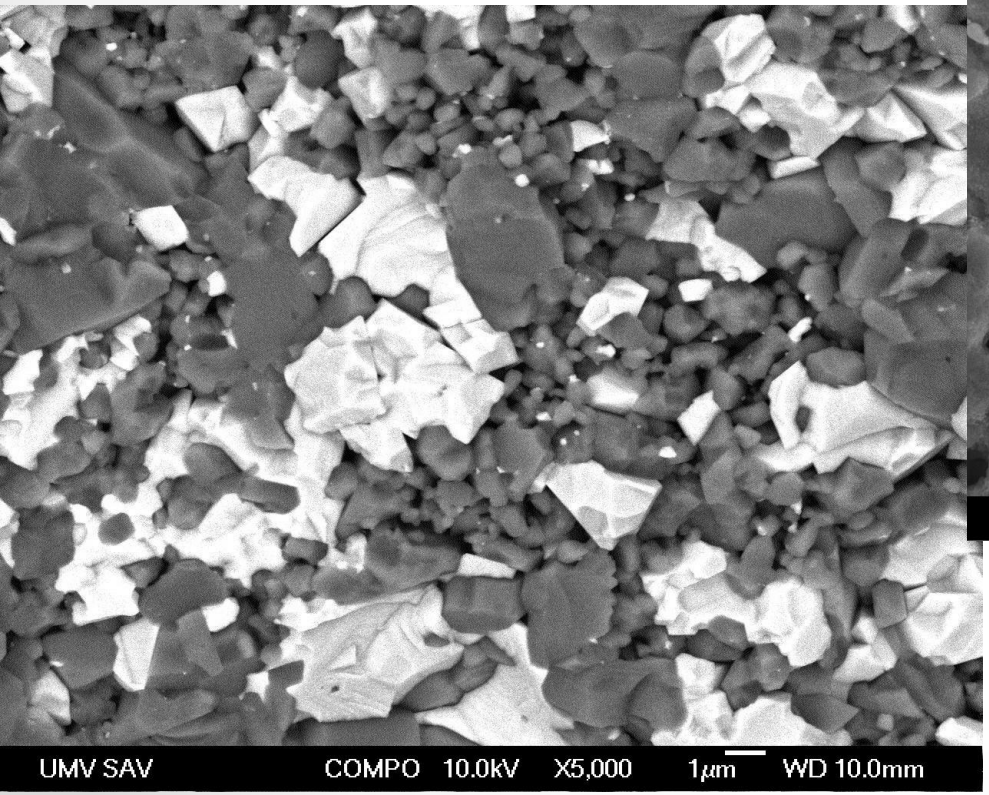




LASER:

v = 10 mm/s

Heat affected zone, microcracking, brittle facets



Conclusions SiC-TiNbC

- Three composites SiC-TiNbC were prepared with good microstructure and satisfactory porosity.
- Measured HV1 increased with increasing amount of additives from 20.10 ± 1.4 GPa for 30 % additives of TiNbC up to 27.39 ± 1.94 GPa for 50 % additives of TiNbC. At various indentation loads strong load-size effect was identified.
- Measured fracture toughness slightly increased, from 2.52 ± 0.67 MPa.$m^{1/2}$ for 30 % additives of TiNbC up to 3.21 ± 0.53 MPa.$m^{1/2}$ for 50 % additives of TiNbC.
- Indentation cracks propagated intergranularly and partially transgranularly through the grains in both of the phases SiC and TiNbC.
- H_{IT} (10 mN load) of SiC was 42.33 ± 1.06 GPa, that of TiNbC was 35.73 ± 0.99 GPa.
- E_{IT} of SiC was 553.1 ± 24.6 GPa, and for TiNbC it was 593.5 ± 28.8 GPa.
- Lowest coefficient of friction – 70/30 SiC/TiNbC (around 0.3) by all used forces. Specific wear rate – similar in all materials (10^{-6} mm^3/Nm). Increasing load – more intense microcracking.

Conclusions SiC-TiNbC

- Electric conductivity of basic SiC material is typically around the values of 10 S/m. The conductivity of the composites was at least 3 orders higher and increased with the amount of TiNbC (from 6668.2 ± 657 S/m to 61474.3 ± 8620 S/m). In all cases it was sufficient for EDM.

- Machinability was tested on material with 50% additives by cutting using four different methods: laser, waterjet, diamond wheel, electrospark – big differences in observed cut surfaces

- The material was easily cut by EDM (v = 1.39 mm/min) – the cut was heavily oxidized – further surface treatment necessary.

Conclusions - general

- Densification of materials with carbon nanophases is still a challenge.
- SiC-GPL – 6 % of GPL - increase of electrical conductivity but far insufficient to allow EDM - distribution has to be controlled.
- SiC-GPL - Increase of toughness with increasing GPLs lead to increase of strength for all composites from ˜200 GPa up to 280-300 GPa
- SiC-CNT - Electric conductivity increased with amount of CNT. For C5 a C10 >1000 S/m (1448 S/m and 2873 S/m, resp).
- SiC-TiNbC – electrical conductivity improved without compromising other properties
- SiC-TiNbC – easily cut by EDM, strong oxidation.

Acknowledgement

APVV 15-0014 (ProCor)

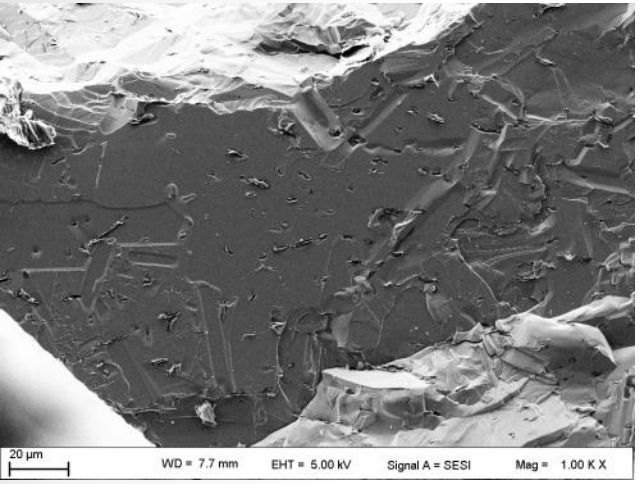
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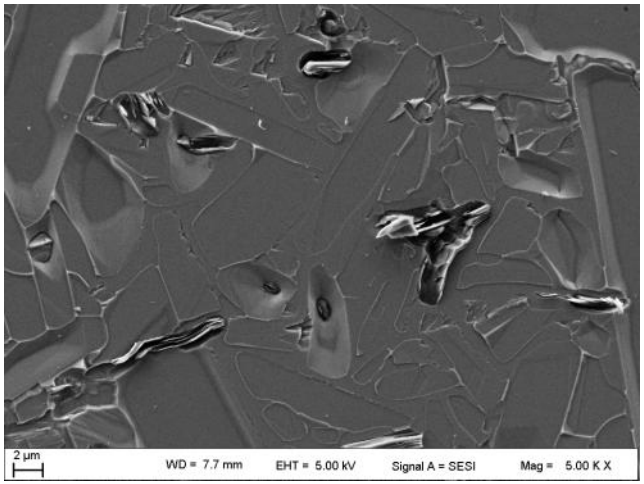
Development of conductive SiC based ceramics

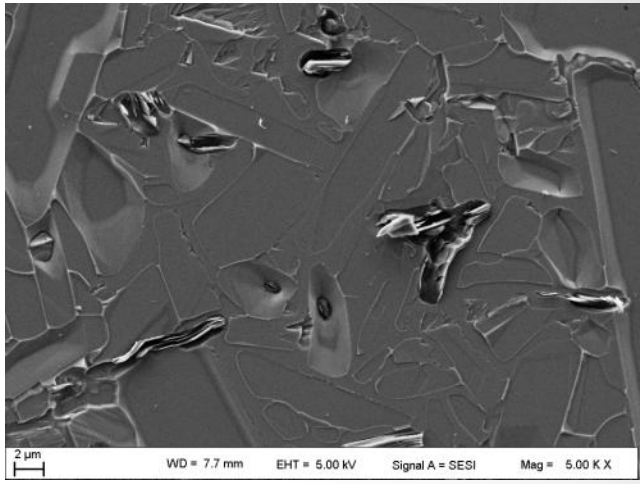
(ConCer)

Thank you

SiC-GPL
fractography







0,5

