State-of-the-Art and Challenges in Ceramic Nanocomposites

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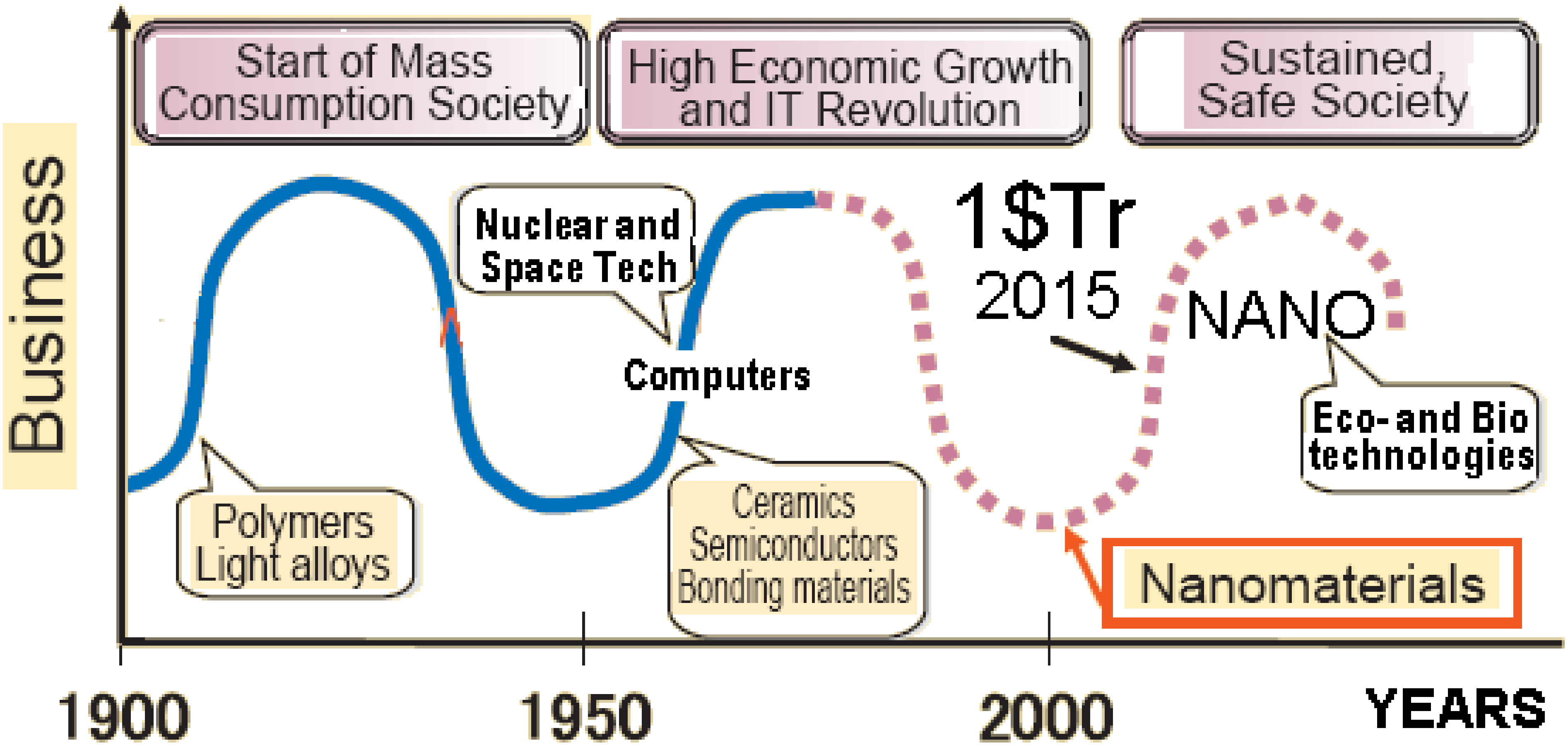
IPMS NAS of Ukraine

Materials Innovation as a Prime Mover of Economic Development



Complication of structure, engineering, atom-scale assembling

increasing number of functions per volume unit

The smaller is the scale,

the more scaled the problems are …

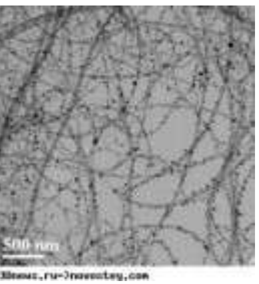
Miniaturization of devises

Size effect in properties of nanosystems

Complicated multifunctional systems, nanocomposites. Self-organization in inorganic systems

Systems which act in «NANO»-scale only, supramolecular- and biosystems

Nanocomposites (definition)



- **The multiphase materials, where at least one of the phases is represented by nanosize crystallite (grain) with the size less than 100 nm, or structures, having regular or stochastic interfaces between different phases. These structures are components of the nanocomposite.**
- **In the wide sense this definition includes porous media, colloids, gels and co-polymers, but most often it is used in the case of combination of bulk matrix filled with nanophase inclusions, different by properties structure and chemical bonding.**
- **The scale limits for instance are:**

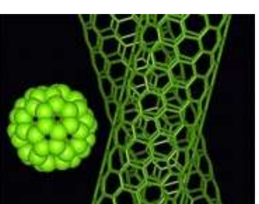
  Less than 5 nm for catalysis,

  Less than 20 nm for transition hard to soft ferromagnetics

  Less than 50 nm for changing a refraction index

  Less than 100 nm for transition ferroelectric to paraelectric,

- In mechanical sense, the nanocomposites differ from conventional composite materials by extremely high ratio of interface area and volume.



Motivations for nanoceramics and

Scope of presentation

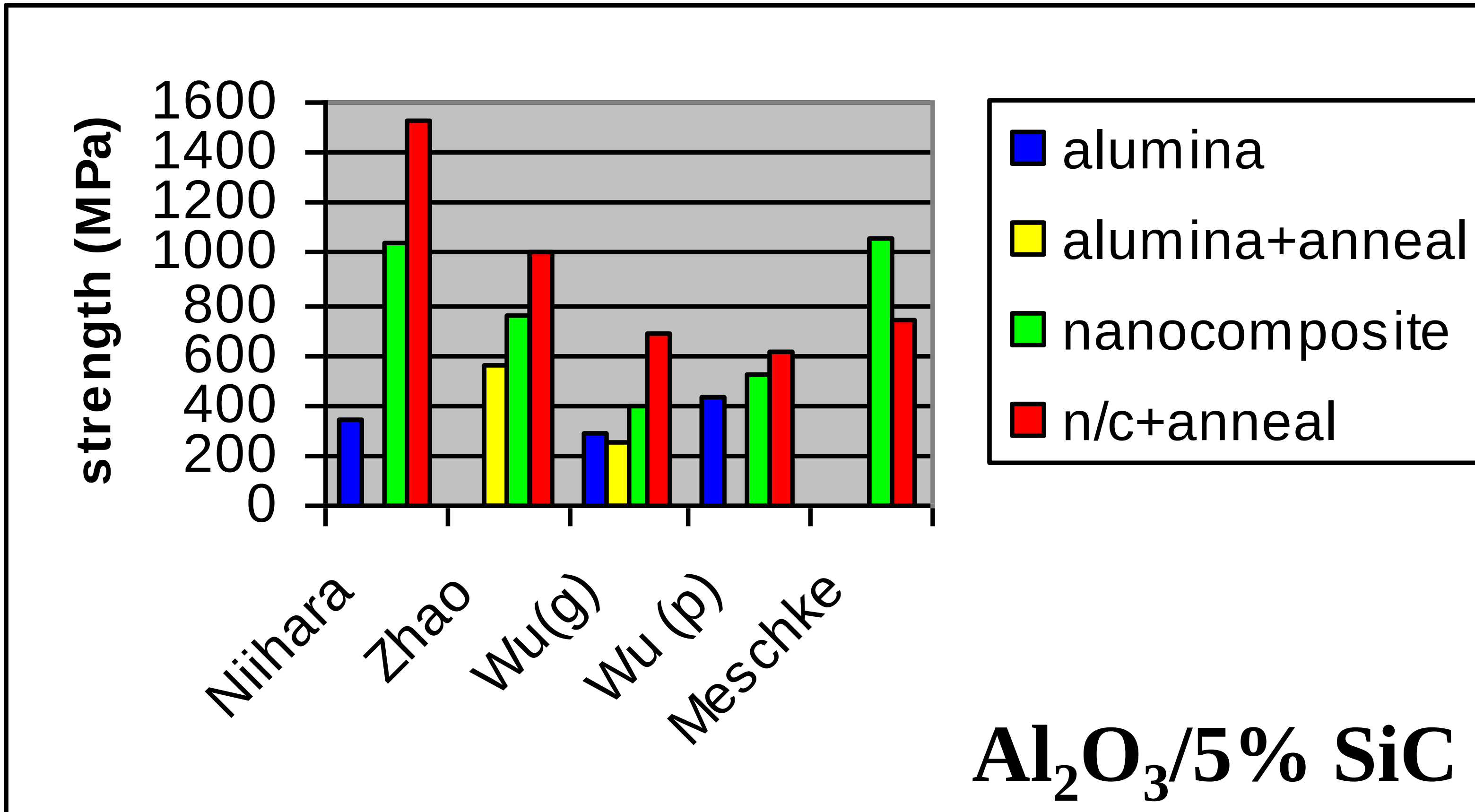
- Manufacturing of 3D fully dense particulate bulk nanomaterials and complex shape parts from them avoiding post-treatment – **sounds like formulation of new segment of market**;
- Improvement of exploitation performance owing to size effect in mechanical and structural properties: hardness, fracture toughness, ductility, wear resistance, strength, superplasticity.
- Cymbate behavior of mechanical properties of nanocomposites as opposed to antibate one in coarse-grain composites.
- Multifunctionality of nanocomposites is real;
- Exploitation most green and fast manufacturing technologies existing nowadays as compared to conventional ones.

Motivations for nanoceramics based on high melting compounds

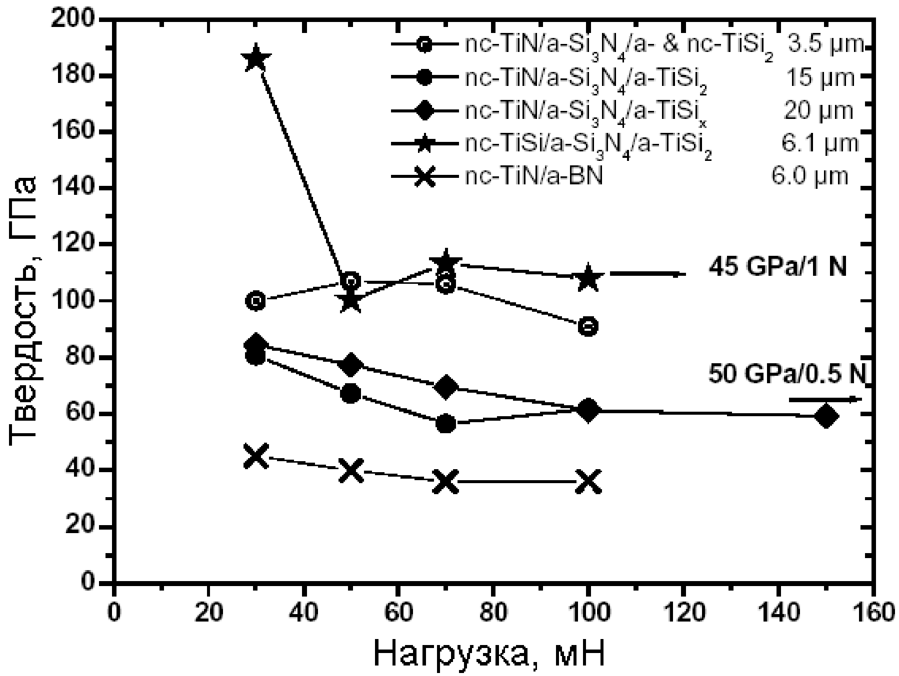
System	Properties and Applications
Si_3N_4-TiN Si_3N_4-TiN-$TiSi_2$	developing wear-resistant materials (ball bearings) with good environmental and biological compatibilities in air and sea water
Si_3N_4-TiC	Ceramic cutting tools SILINIT-R^{TM}
HfB_2–SiC, ZrB_2–$MoSi_2$, ZrB_2–ZrC–SiC TiB_2–WB_2–CrB_2	high-temperature applications in supersound vehicles, corrosion–wear–oxidation resistance are superior. electrochemical processing of aluminium, evaporation boats, crucibles for handling molten metals, thermowell tubes for steel refining, thermocouples sleeves, nozzles, etc.
B_4C-TiB_2, $B_{13}C_2$-SiC	Armored ceramics
TiN-TiB_2	Ceramic cutting tools and wear resistive components

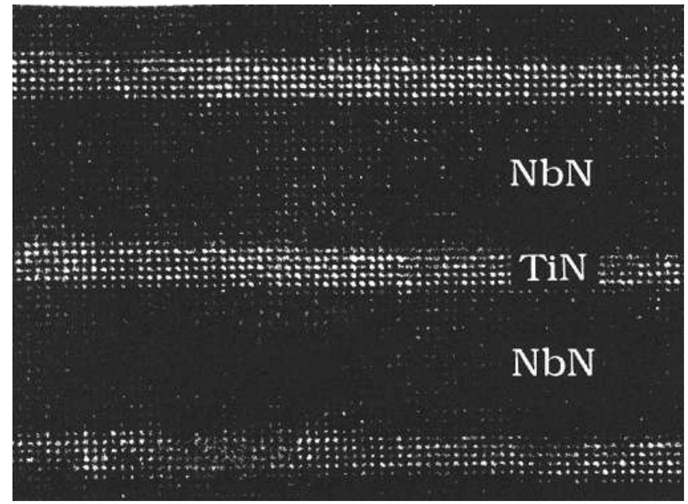
More than 50 systems of high-melting nanocomposites were studied !

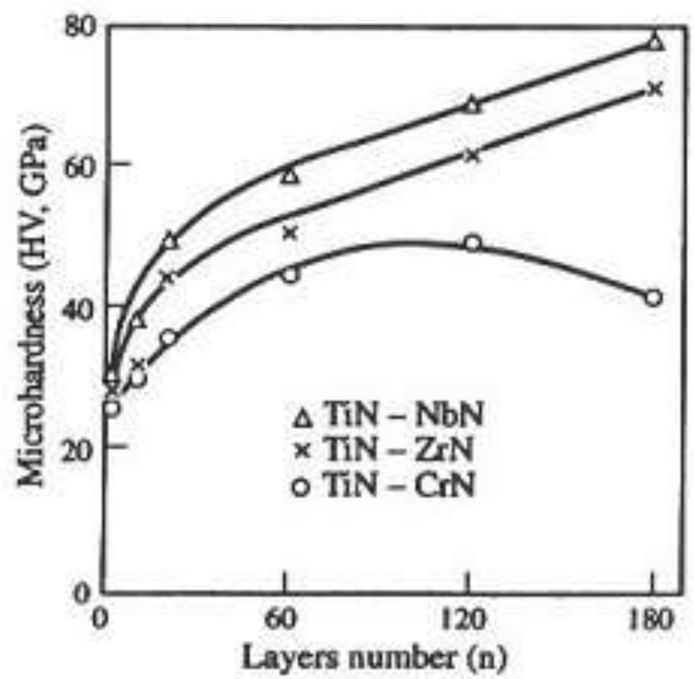
Strength of nanocomposite Al_2O_3 /5% SiC (~1300°C, in air or in Ar)



Composite and multilayer films and coatings of high melting materials





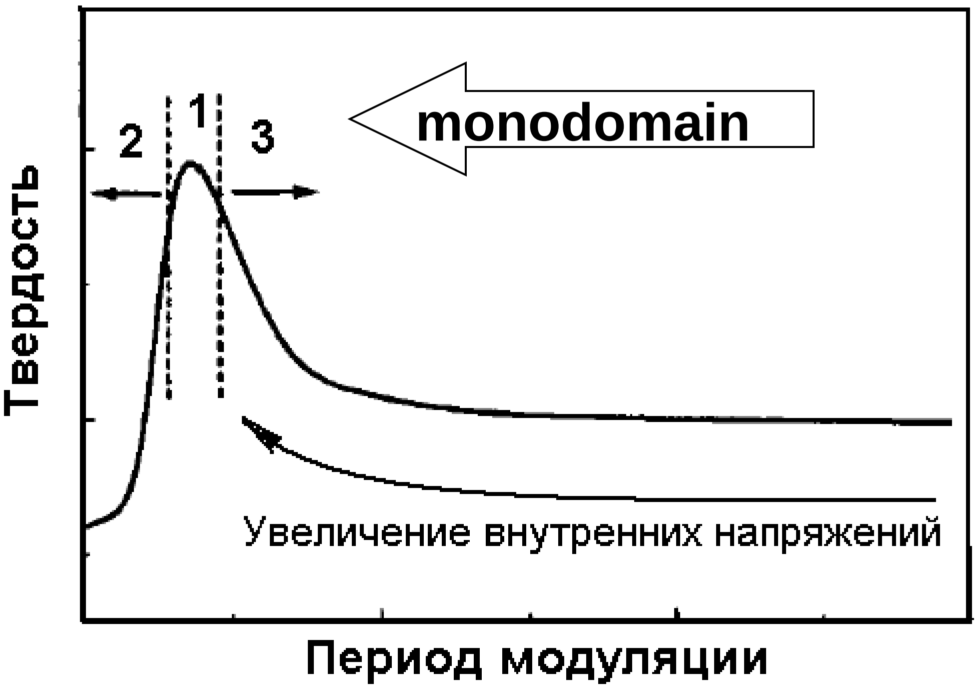


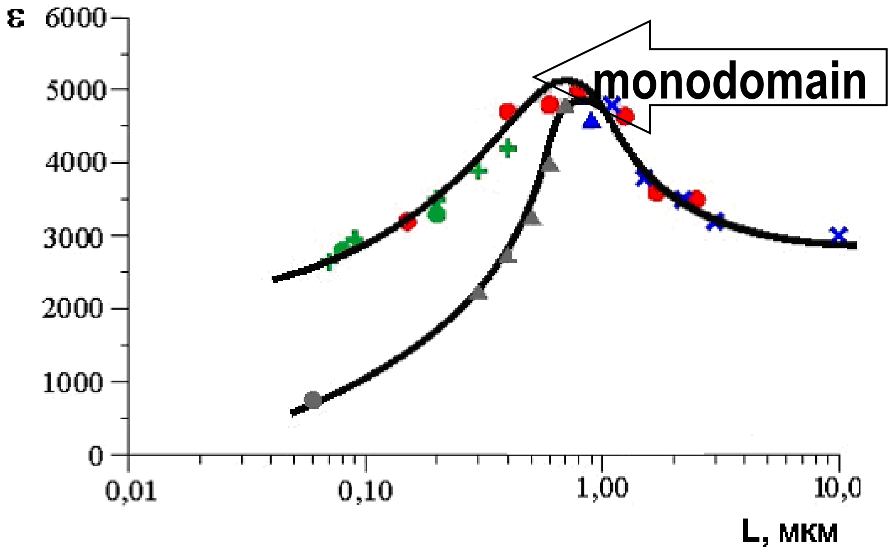
Veprek et al Mater. Res. Soc. Symp.Proc. 697 (2003)

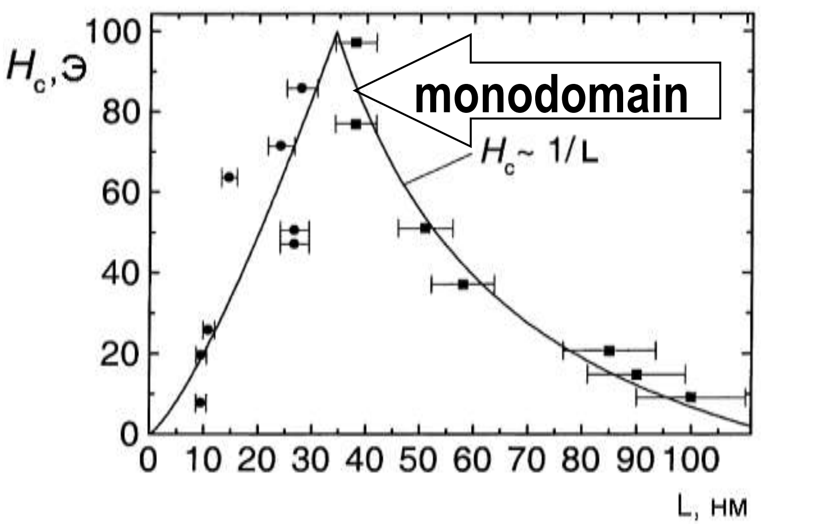
Nanocomposites demonstrate unique fundamental features:

- Grains/layer are in complex stress state at least in one dimension
- Substantial portion of atoms are located on interfaces and in triple junctions, and even in one-phase material we deal with two phase material.

Stresses due to mismatch lattice parameters, thermal expansion differences are compensated by elastic deformation of layers / grains







Stresses of 1 - 10 GPa

Boundaries – crystalline and amorphous

Average size of TiN nanocrystallite of 9 nm corresponds to 16–20 mol% of amorphous Si3N4, and maximal hardness nc-TiN/a-Si3N4 - 50 GPa.

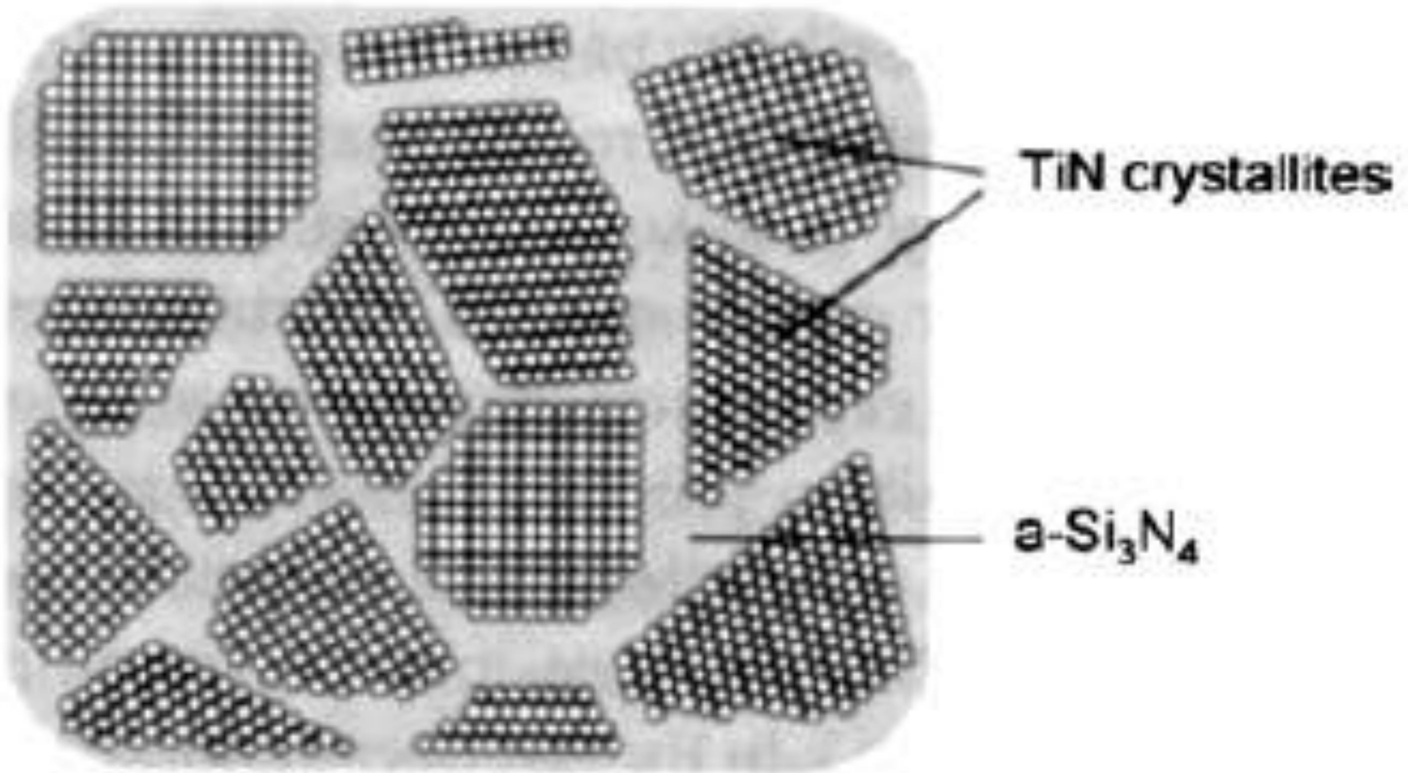


Figure 10. Schematic representation of the nc-TiN/a-Si_3N_4 nanocomposite consisting of TiN nanocrystals embedded in an a-Si_3N_4 amorphous matrix. Reprinted with permission from [166], R. Hauert and

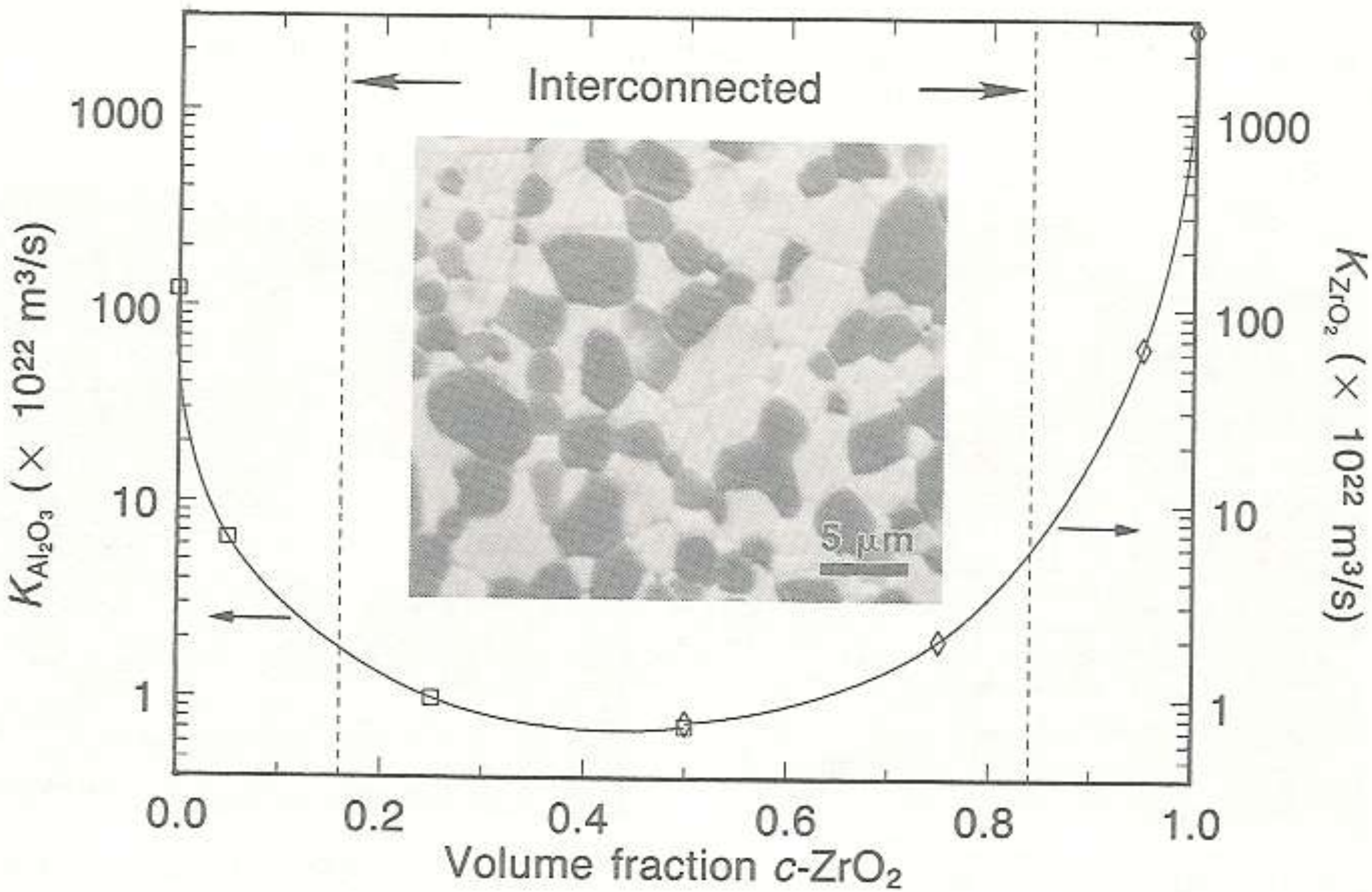
Experiment helps us to understand that…

To achieve superhardness, LACK of DISLOCATIONS – is the most important quality than chemical bonding.

- **Nanosize crystals are free of dislocations or keep small number of them.**
- **Migration of dislocations through interfaces is forbidden and dislocation loops do not work in the nanosize domains.**

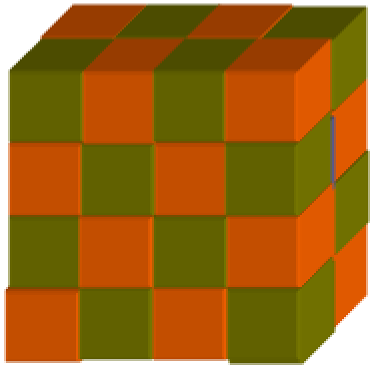
- **Orovan mechanism: sliding of dislocations has limited operation inside grain or layer only.**
- **Keller mechanism: migration of dislocations is forbidden between grains or layers due to share modulus gap.**
- **Mechanism of coherent action of stresses: migration of dislocations is forbidden due mechanical stresses changing the sign on interfaces.**

Grain growth kinetics in two phase Al_2O_3/ZrO_2 nanocomposite

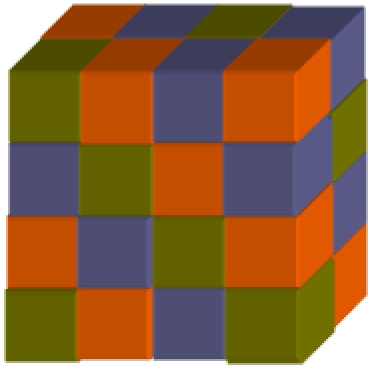


Experimental kinetics of grain growth corresponds to Ostwald law $d^3 - d_0^3 = Kt$, i.e. grain growth is retarded.

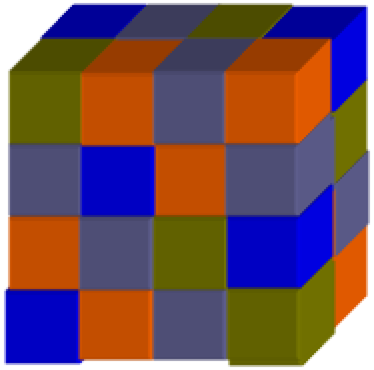
How many components should be in the nanocomposite to prevent grain growth ?



Two?



Three?



More ??

Would there be an advantage of three or four phases over 2 phases

Diffusion distance for Ostwald ripening would be further

Continuous creep phase may be eliminated

Answers must be found experimentally

R. Cannon, Rutgers, 2004

Challenges of nanoparticles consolidation

- **Nanosize of particles escalates difficulties of their consolidation into bulk nanomaterial.**
- **Huge specific surface area and ability to form aggregates seriously narrow our choosing the reliable methods**
- **We need new methods of mixing !!! and synhesis !!! Mechanical mixing of nanoparticles cannot be effective any more ;**
- **template synthesis looks attractive…**
- **Self-organization and self-assembling «particle –to–particle or rod-to-rod in the colloidal systems» these approaches are on leading edge;**
- **New consolidation techniques are necessary.**
- **Control of interfaces is a key problem.**

How to «assemble» nanocomposite into bulk material ?

Pyrolysis of silicon-polymers, and polymers filled with nanoparticles of other phases (homogeneous matrix) + rapid prototyping technology

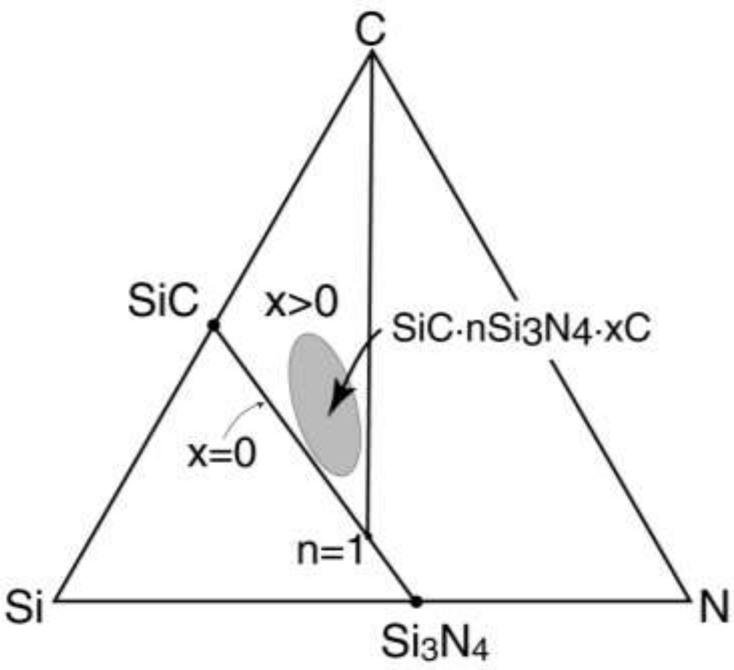
Assembling of composite nanoparticles in electrophoretic bath under strong magnetic field

Reaction-driven fast sintering techniques of multicomponent systems

Drop-on-demand quantization of substances of different «colors», ink-jet printing with droplets of 10^{-13} liter in size containing small amount of substances

Pyrolysis of silicon-based polymers

Several features of SiCN based nanocomposites



- *"Amorphous/Nano"*
- Semiconductor (till 1350°C)
- Stable to oxidation
- Ultra-low creep
- Shock resistive

What is the structure to provide such a behavior?

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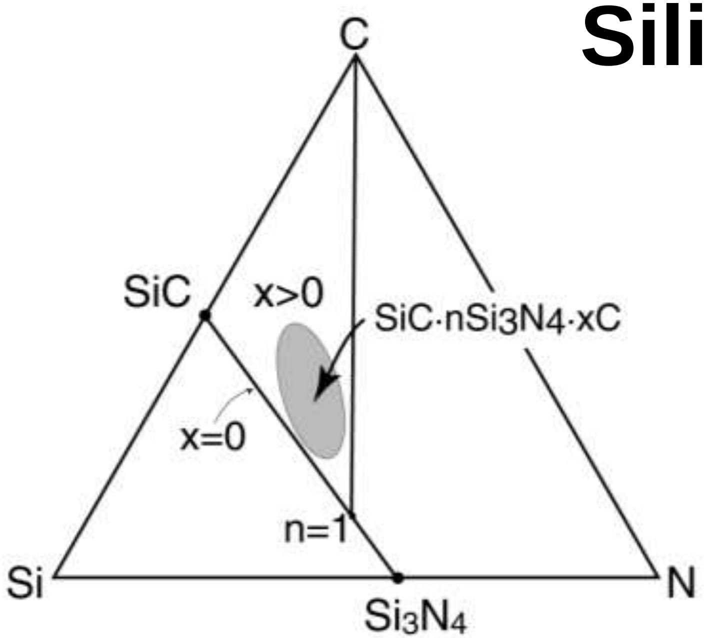
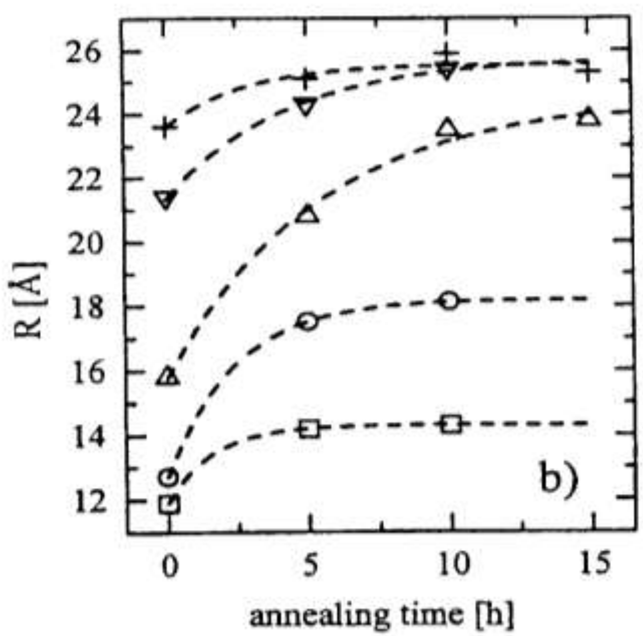
Silicon carbonitride (SiCN)

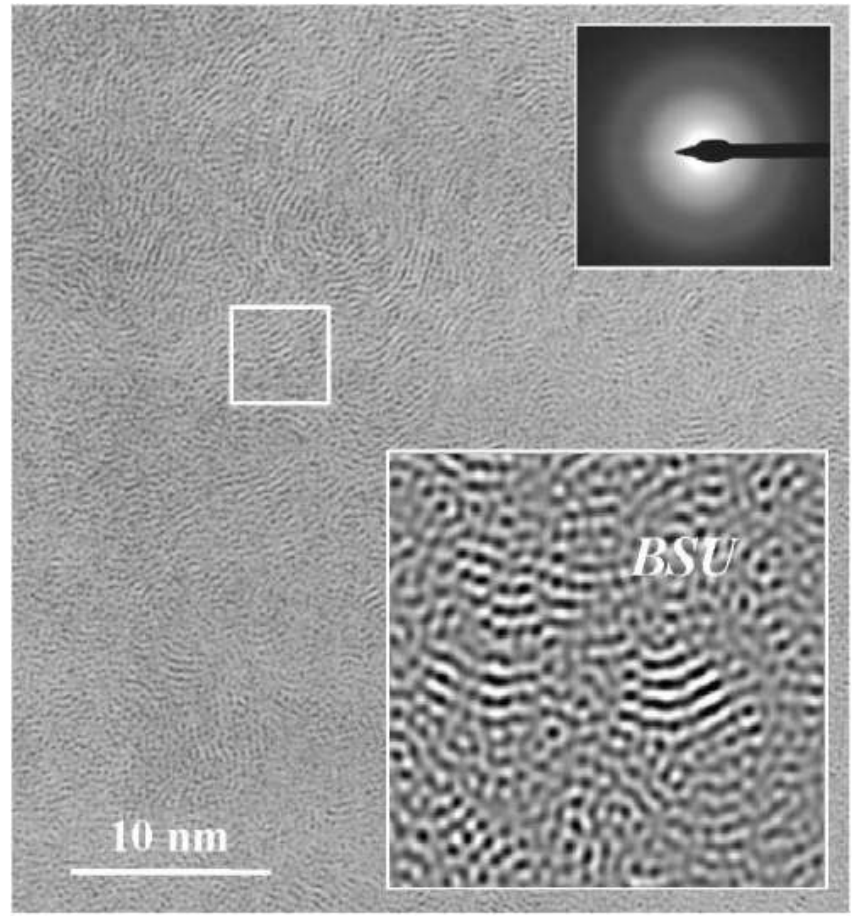




1600 C

1200

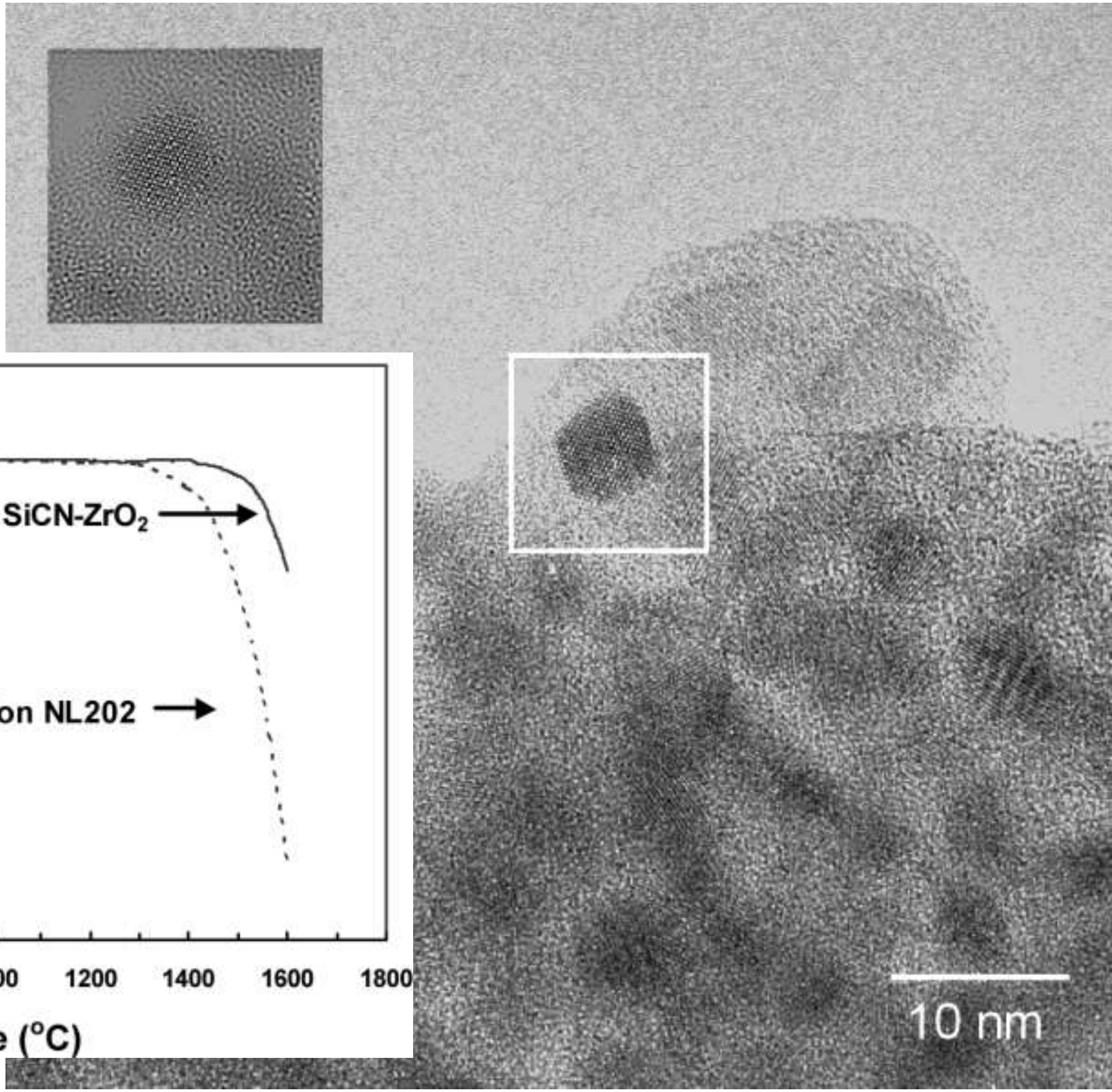
1000

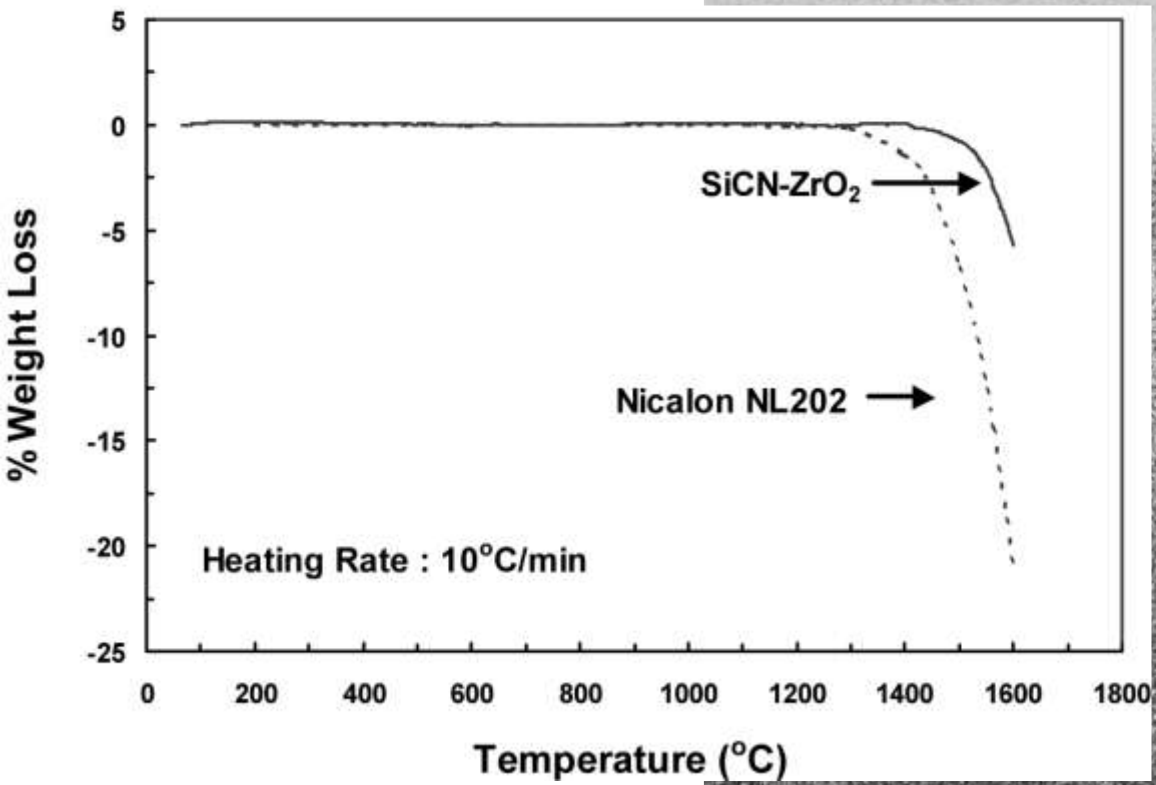


H.-J. Kleebe (CSM)

SAXS+SANS grain sizes

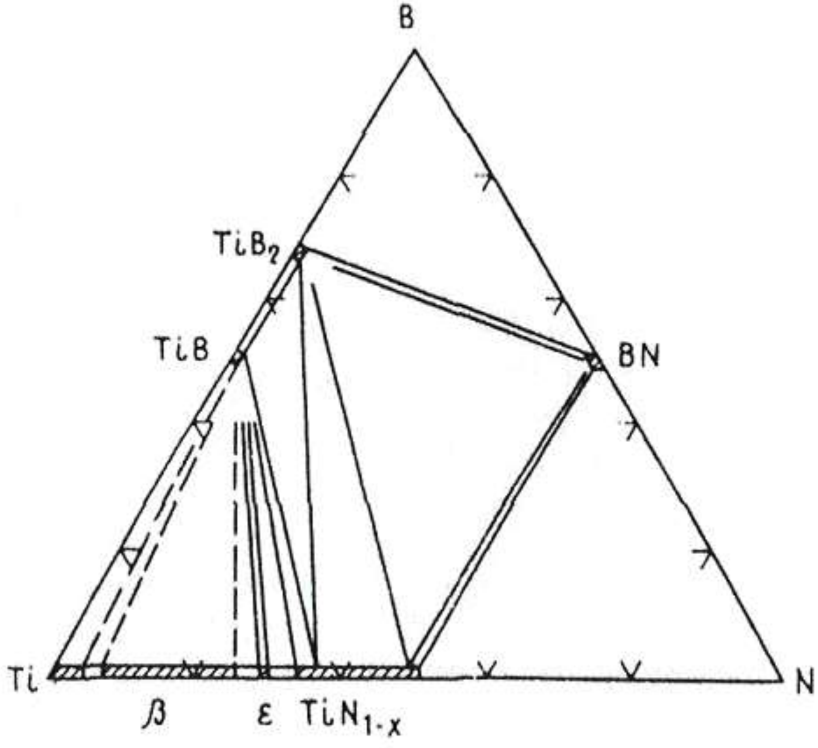
SiCN – ZrO_2 Nanocomposites





Large reserves belong to multicomponent systems

Hardness of 40 GPa can be achieved in the system Ti–B–N including hard phases TiB_2 TiN and c-BN. The higher hardness of 57 GPa for the $TiB_{05}N_{05}$ (TiN/TiB2) composite. The magnetron sputtering of the target Ti/h-BN using bias voltage of −150 V at temperature 400 °C.

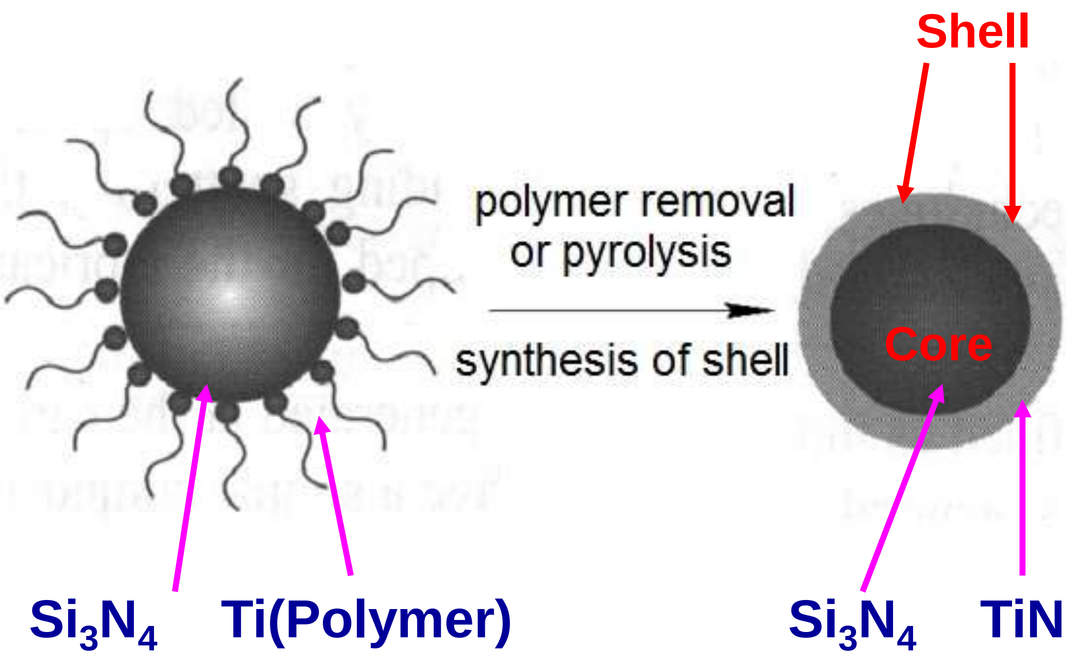


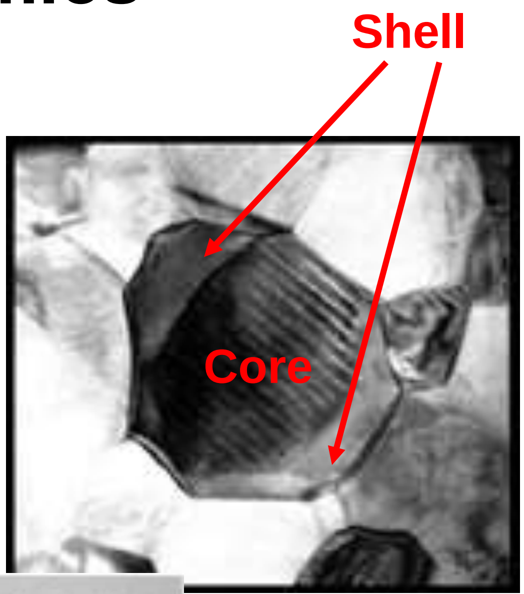
Equiatomic ceramics is prespective !?

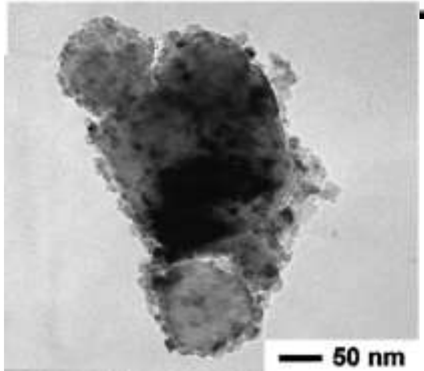
Synthesis of in-situ nanocomposite powders using colloidal processes

The structural mimicry effect achieved

Powders - Ceramics



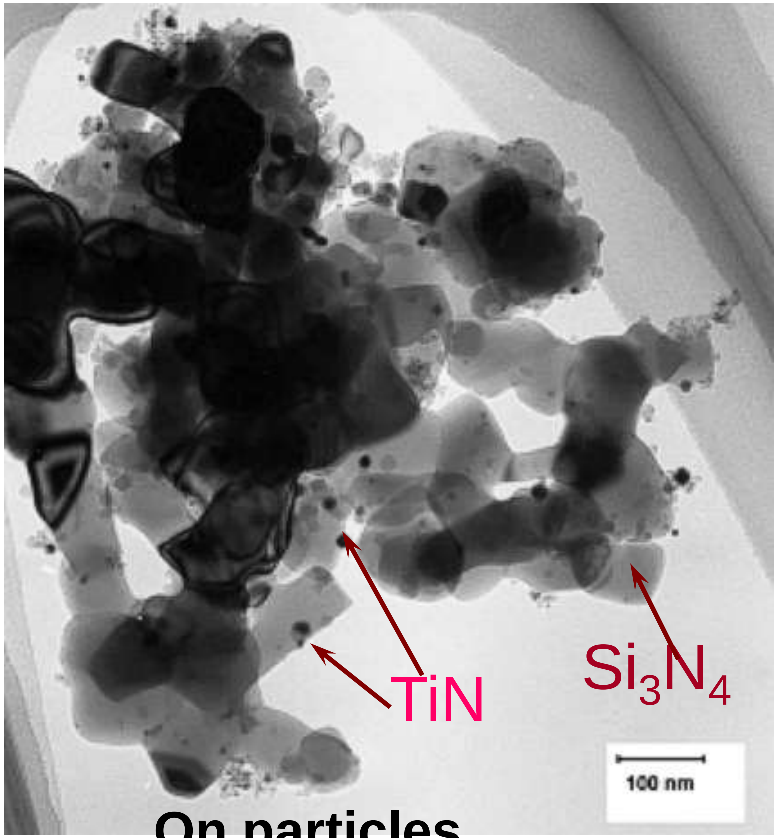




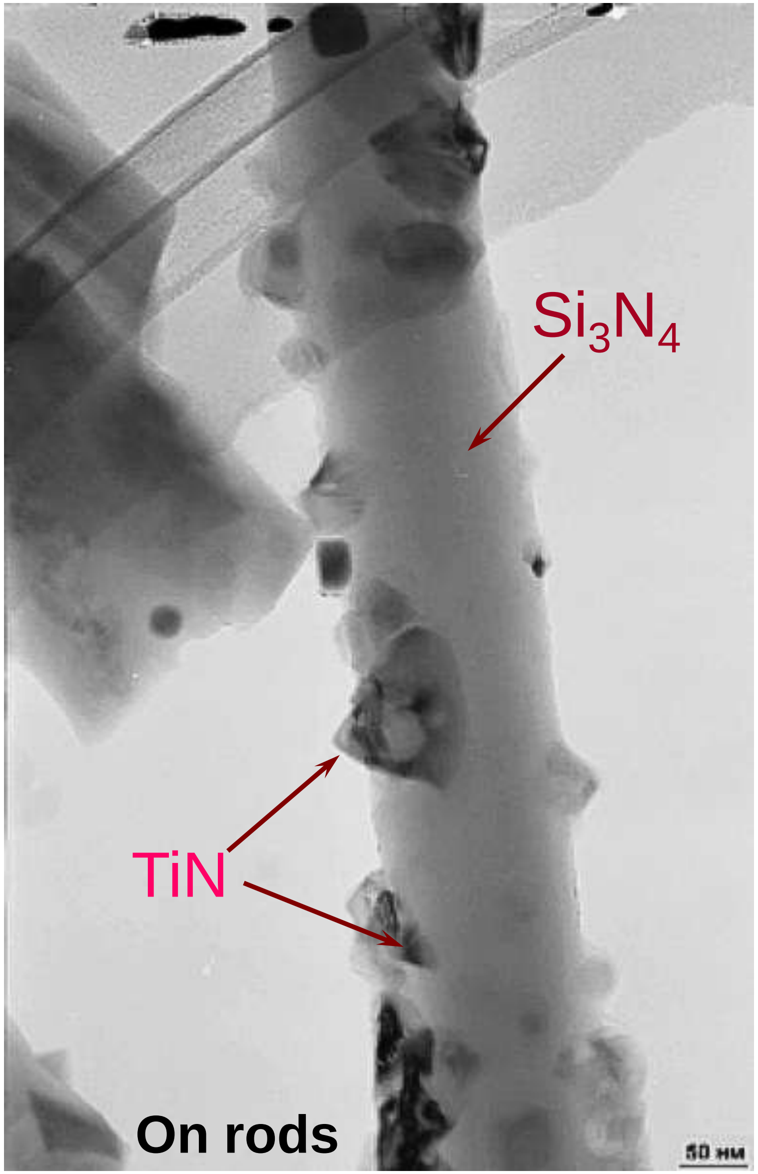
A. Ragulya

H. Kawaoka

In-situ nanocomposites Si_3N_4-TiN



On particles



Nanoparticles of TiN were synthesized on a surface of mesoporous nanorods or nanoparticles Si_3N_4

A. Ragulya et al, Powder Met.&Metal Ceram. (2008)

Sintering of nanopowders

Features of nanopowder's consolidation

Observation:

Sintering of nanoparticles occurs mainly on heating stage

Conclusions:

Non-isothermal techniques are most prospective

Choice of heating rate is becoming principle

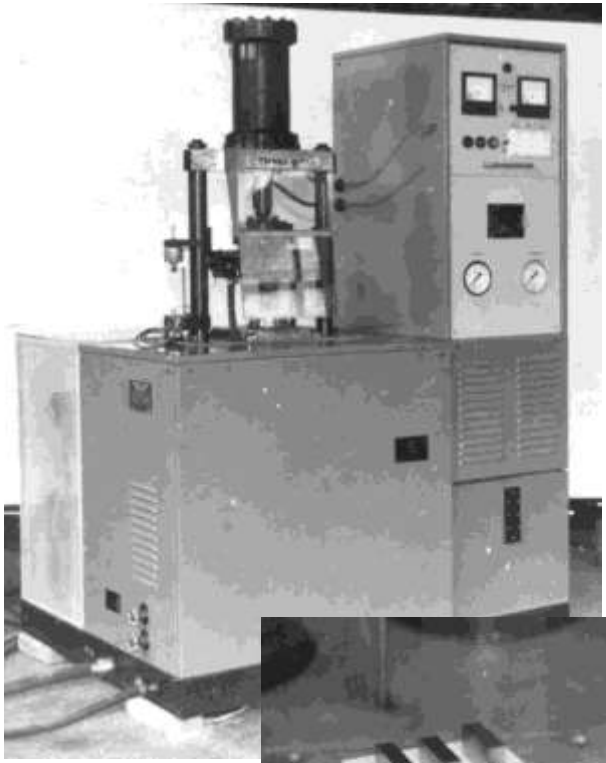
Competition of sintering mechanisms defines heating rate: the rapid rate sintering on the initial stage, variable moderate heating rates on the intermediate stage and finally slow heating.

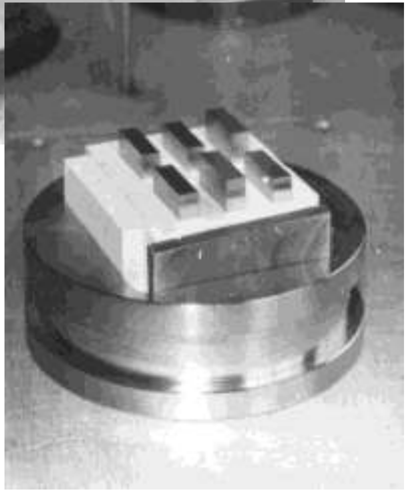
Temperature gradient results in shrinkage rate and density gradients !

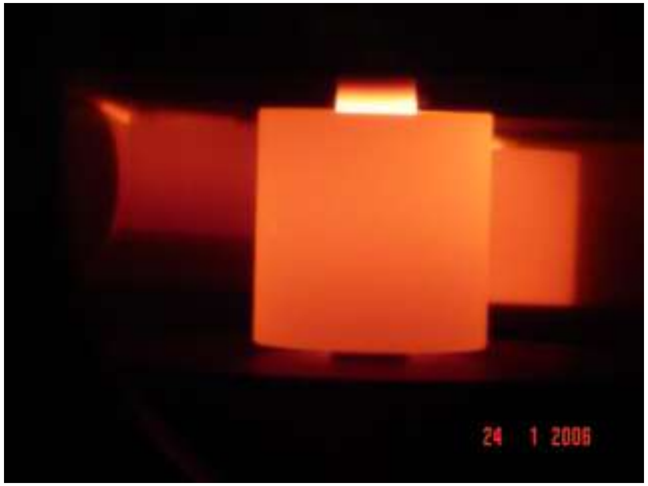
FAST/SPS works exactly in this area.

Progress of SPS installments:

“Strum” at IPMS in 70-th “Dr.Sinter” at NIMS and FCT HPD25 at IKTS now







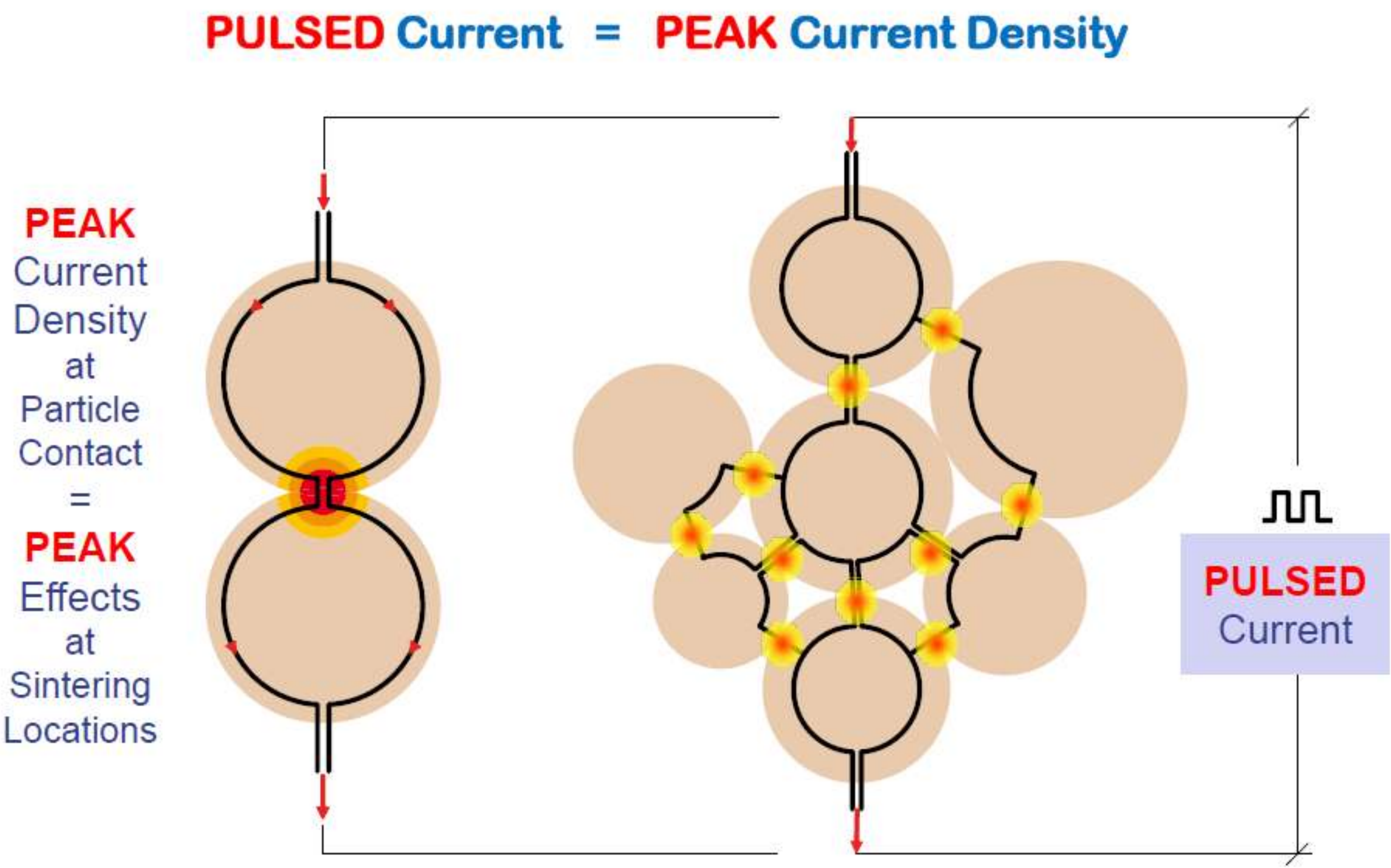
Experimental data on Spark Plasma Sintering of nanoscale powders.

Material	Particle size, nm	Pressure, MPa	Temp-re °C	Heating rate, °C/min	Sintering Duration, min	Relat. density, %	Grai size, nm
Fe-Al		**70**	**~1100**	**-**	**< 1**	**93-98**	**30-50**
Fe-30 at.% Co	**10-15**	**60**	**900**	**N/A**	**5**	**95**	**30**
ZrO_2	**10**	**< 70**		**2 – 10**	**<5**	**95 – 97**	**30 – 80**
AlN	**10**	**22**	**1600**	**160**	**5**	**99.5**	**<100**
Al_2O_3-(5-20%) SiC		**40**	**1100 – 1500**	**200**	**5**	**>99**	**>100**
Al_2O_3	**15**	**63**	**1000-1250**	**300**	**3**	**>98**	**300 – 1000**
$BaTiO_3$	**30**	**100**	**800 – 1000**	**200**	**2 – 5**	**97**	**50 – 100**
$BaTiO_3$	**13**	**50**	**900**	**200**	**0-3**	**96 – 99**	**200 – 700**
MgO		**150**	**800**	**300 - 400**	**5**	**91-97**	**30 – 70**
CeO_2 **$Ce_{0.7}Sm_{0.3}O_2$** **YSZ (8%)**	**7** **8** **6.6**	**600** **610** **530**	**625** **750** **850**	**200** **200** **200**	**5** **5** **5**	**>98** **>98** **>98**	**11 – 13** **16 – 17** **16 – 18**
Al_2O_3 – (5об.%)SiC	**5/70**	**40**	**1450**	**600**	**2-3**	**99**	**-**
SiC/Si_3N_4 (synthesis from polymers)		**63**	**1600 – 1700**	**100**	**10**	**< 96**	**70-300**

Features of Spark Plasma Sintering

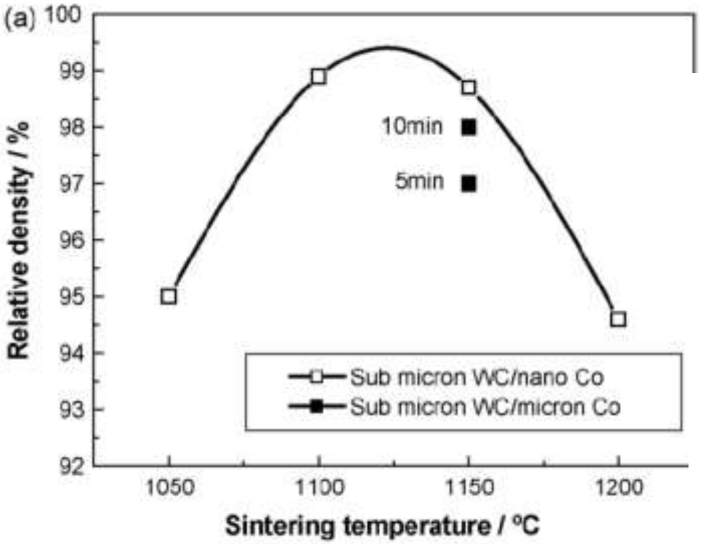
1) generation of local melt pool and it’s effect on heat- and mass-transport;
2) combined effect of external fields on densification and phase formation in particulate system;
3) influence of electric current in the near surface layers of dielectrics, conductors and semiconductors, so called “skin-effect”;
4) the SPS is rapid sintering process with heating rate exceeding 100 °C/min; rapid rate heating rises a problem of non-uniform temperature distribution throughout the sample – however, avoiding large temperature gradients is possible;
5) SPS is capable of sintering difficult-to-sinter materials such as tungsten carbide and hafnium diboride with relative ease and without the benefit of sintering aids;
6) the SPS is available for materials with various chemical bonding.

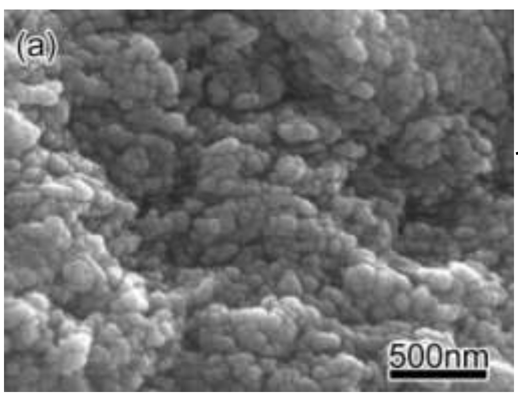
Features of Spark Plasma Sintering

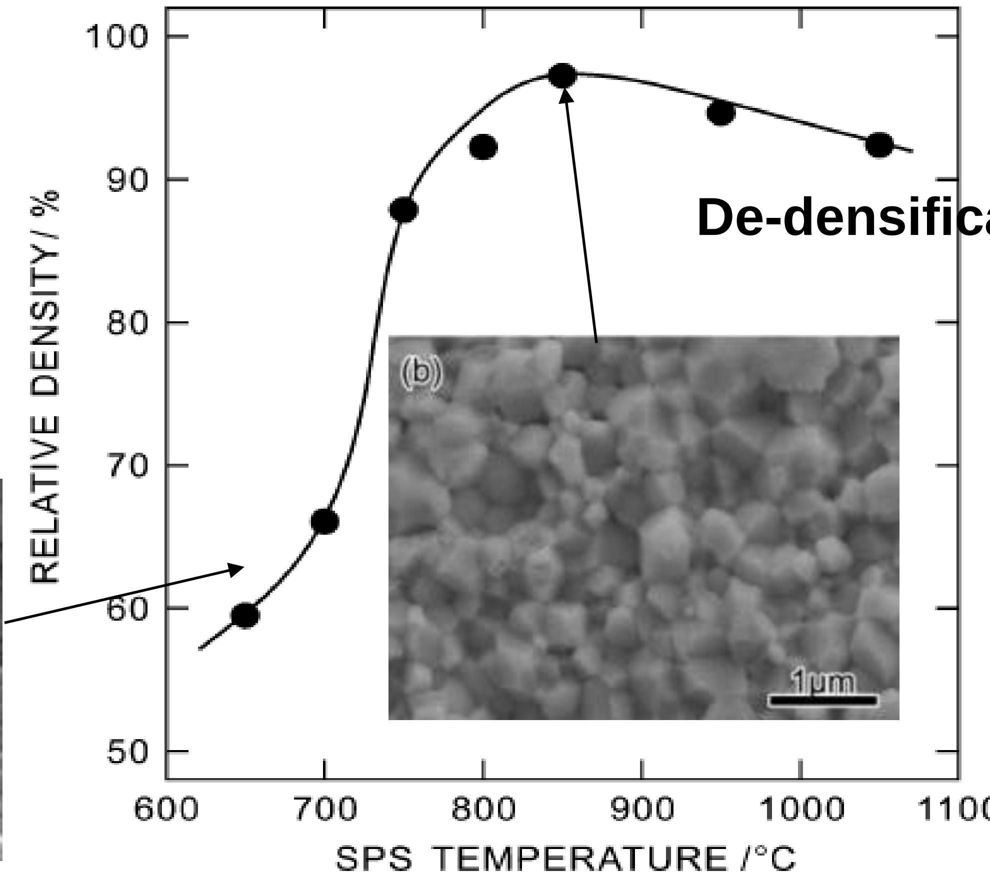


FCT presentation, Dr. Hennicke

Influence of Temperature and Overheating during SPS





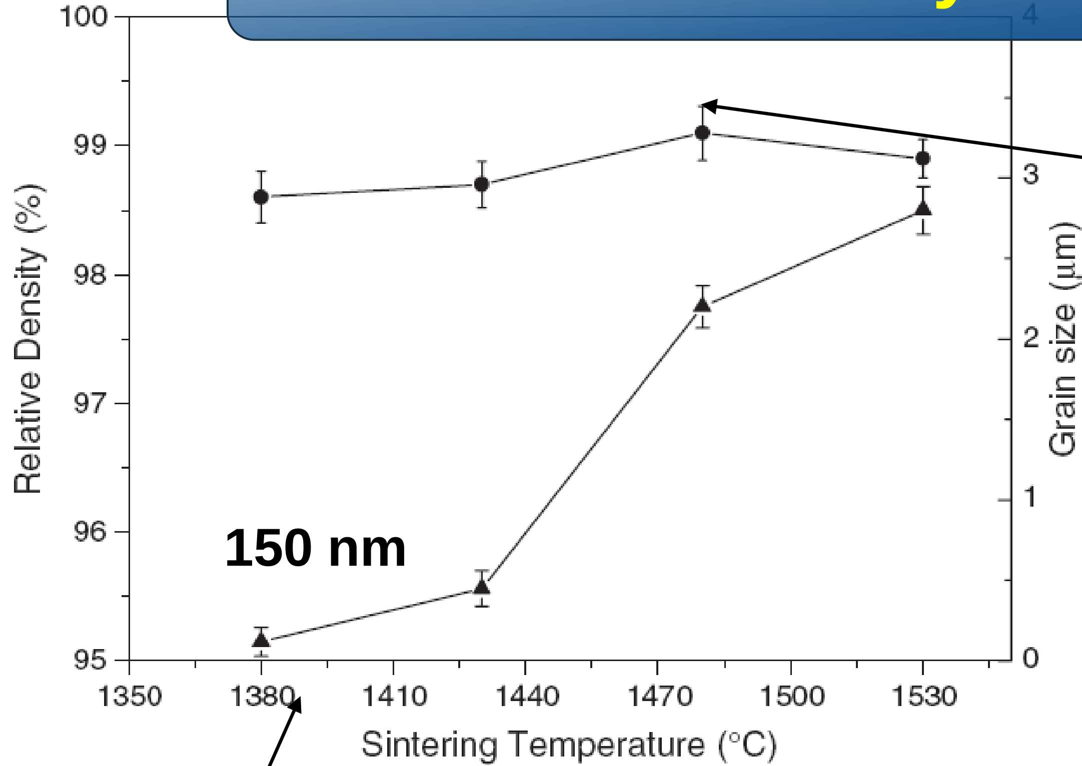


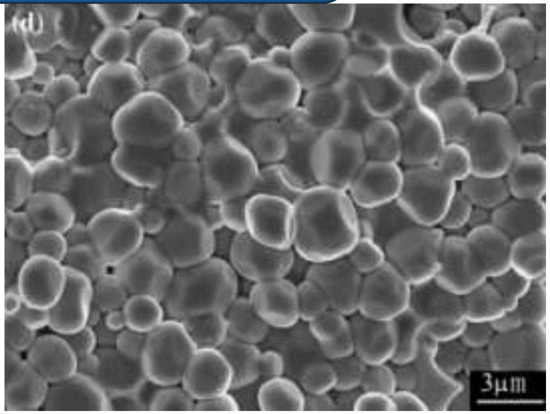
De-densification

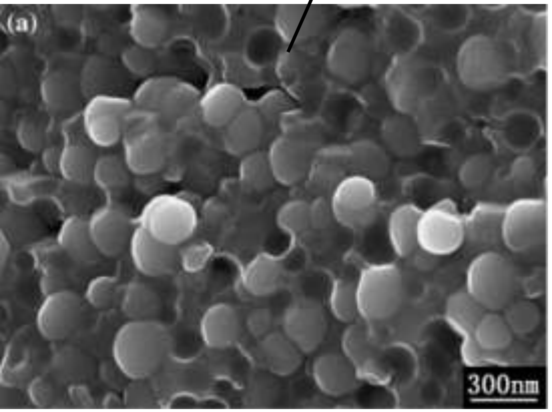
Choice of heating rate is important (shown that it's important to heat slow 8-20 C/min to get full density and maintain smallest grain size)

H.Yoshida et al. J. Amer.Ceram.Soc. 2008

SPS of nanocrystalline Yttria



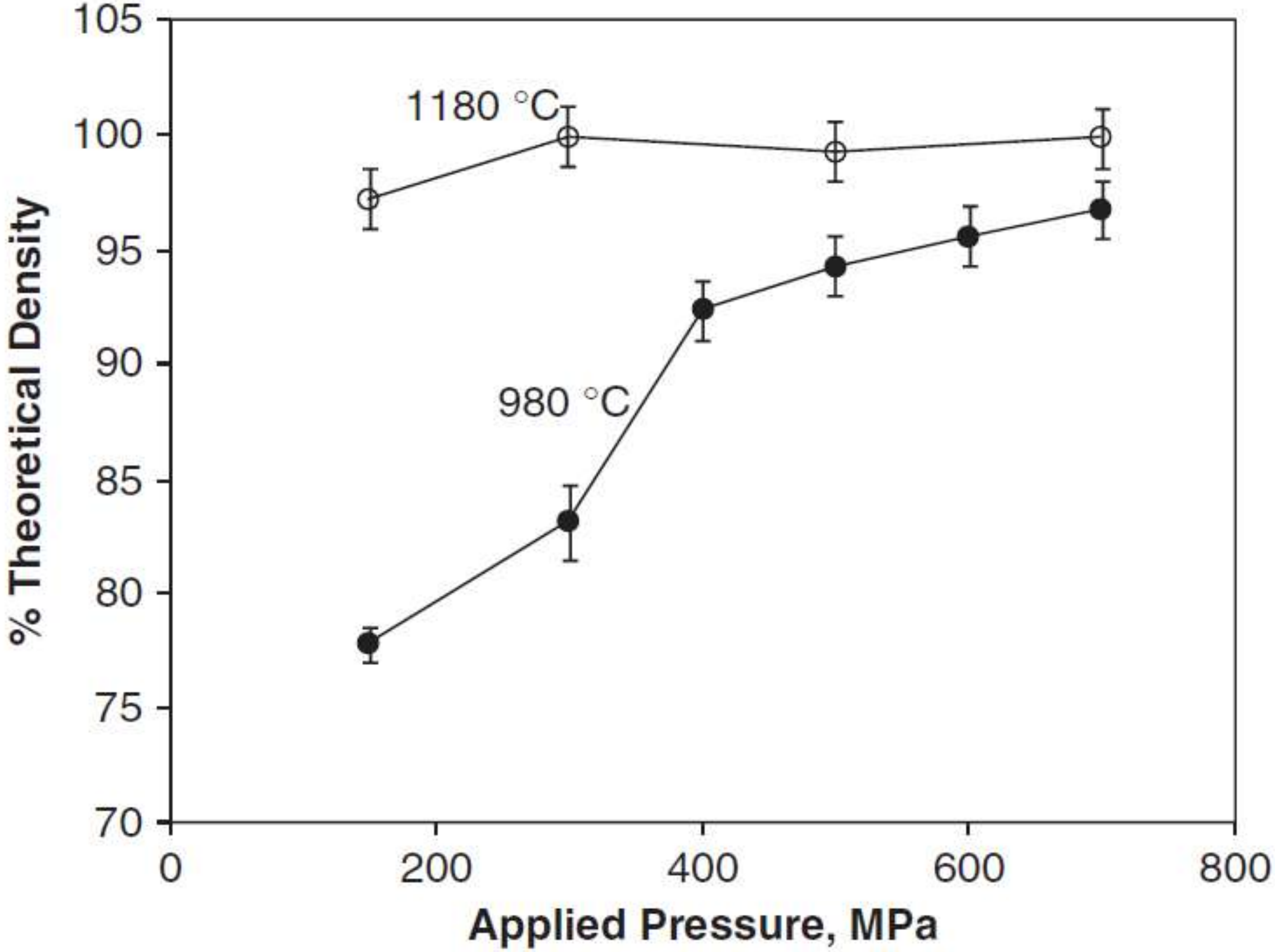




Particle size of 19 nm (shown fast heating rates 100-400 C/min to get full density) – heating rate has to correspond thermal conductivity

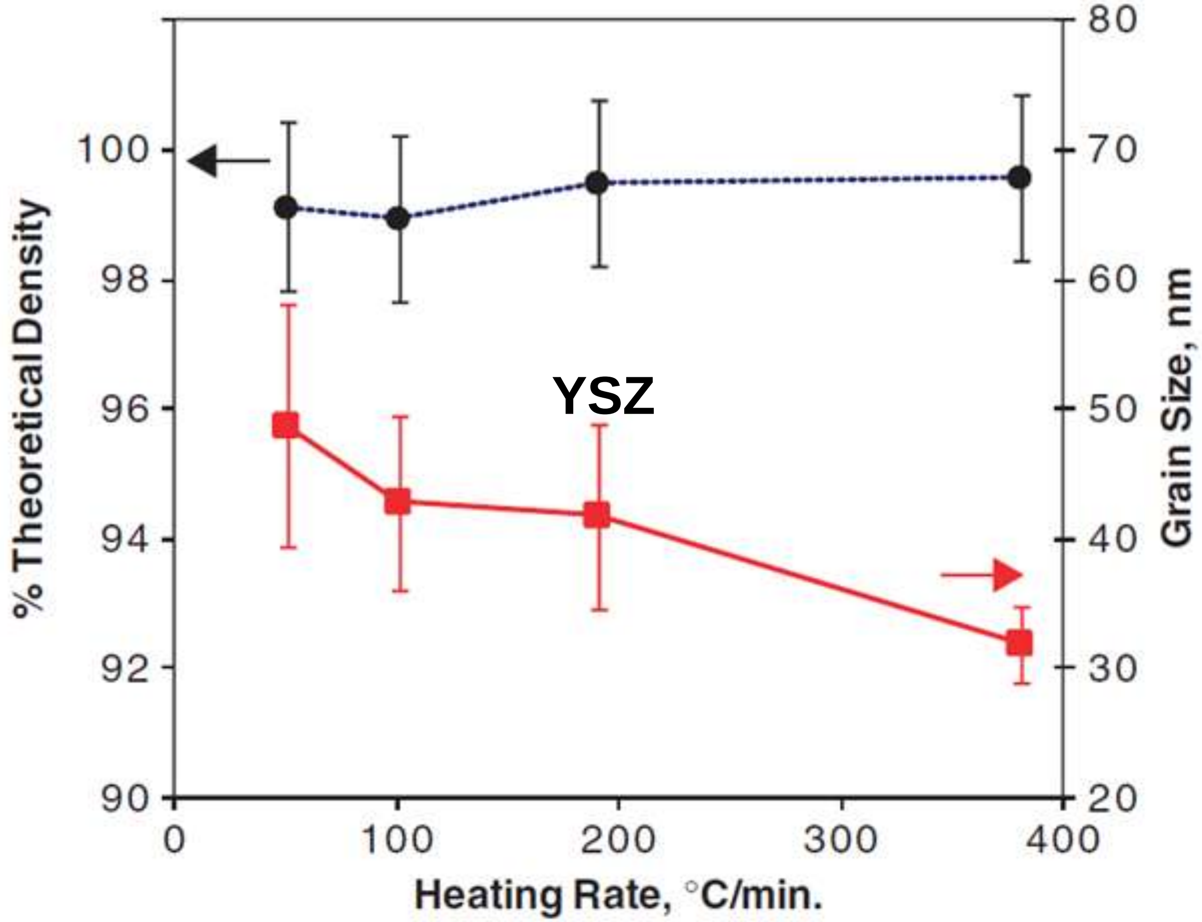
L.Chen et al. J. Amer.Ceram.Soc. 2006

At the higher temperature, the relative contribution of the pressure becomes less significant.



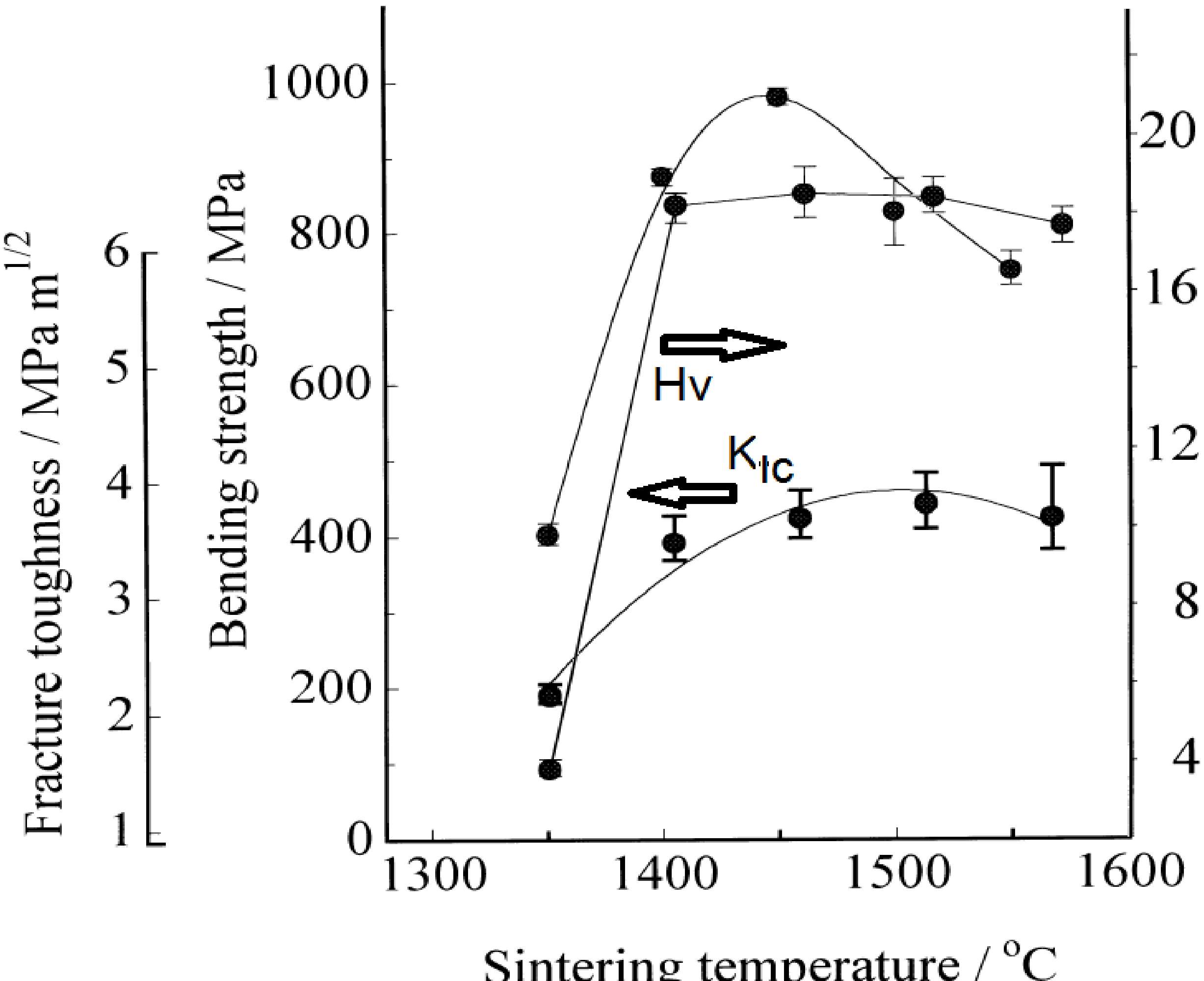
D.V. Quach et al. Acta Mat. 2010, 58

Effect of heating rate on density and grain size



D.V. Quach et al. Acta Mat. 2010, 58

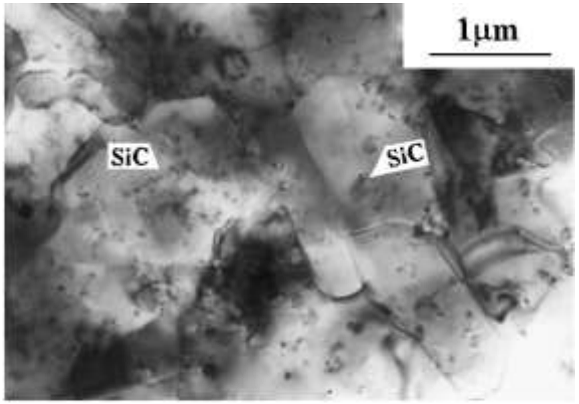
Cimbate behavior of mechanical properties for SPS-prepared 5%SiC - Al2O3 nanocomposites



L.Gao, et.al. JECS, 19, 1999

SiC particles coated with amorphous alumina;

Heating rate: 600 degr./min

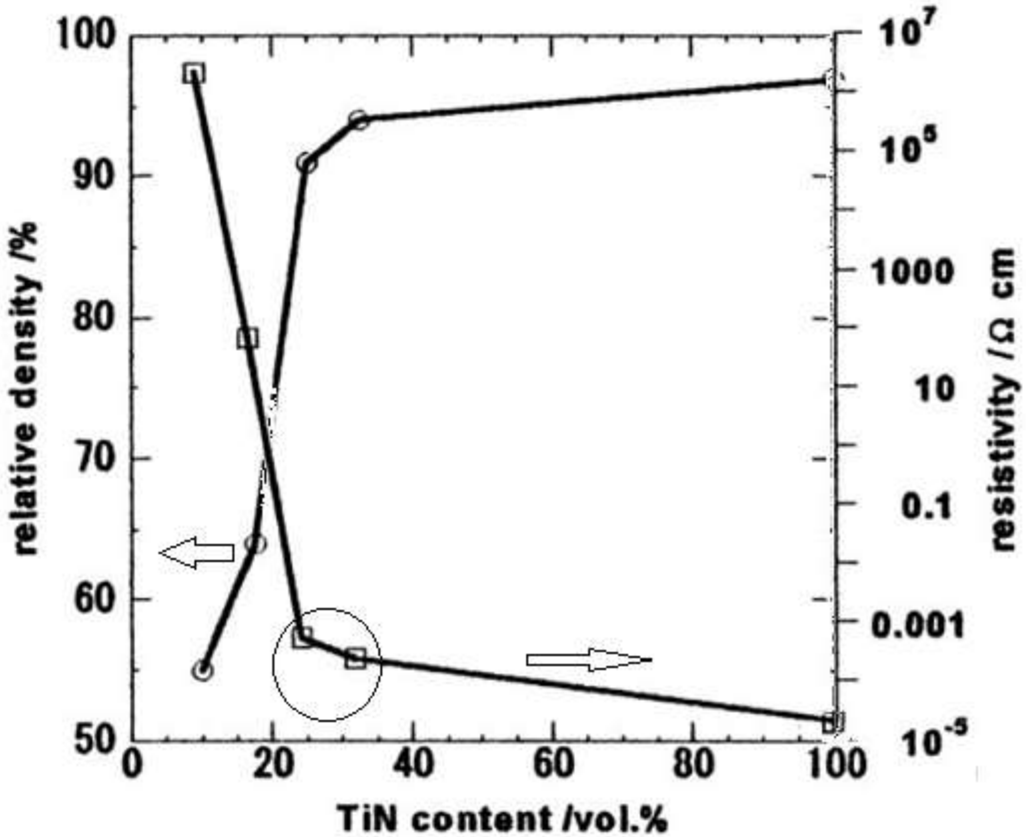


Nanocomposites based on

Si_3N_4-TiN system

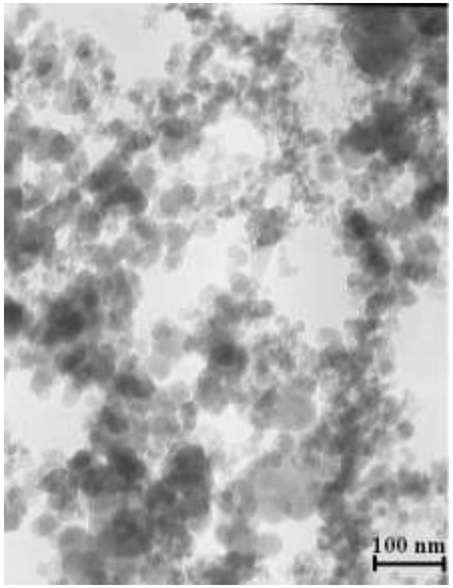
Sinterforging Si_3N_4-TiN

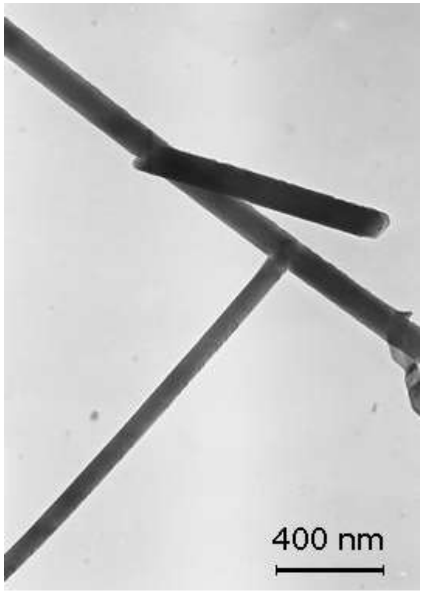
Density and conductivity of Si_3N_4 – TiN ceramic nanocomposite

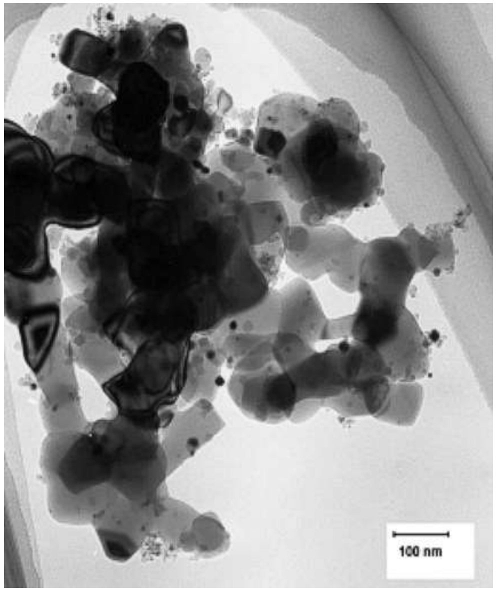


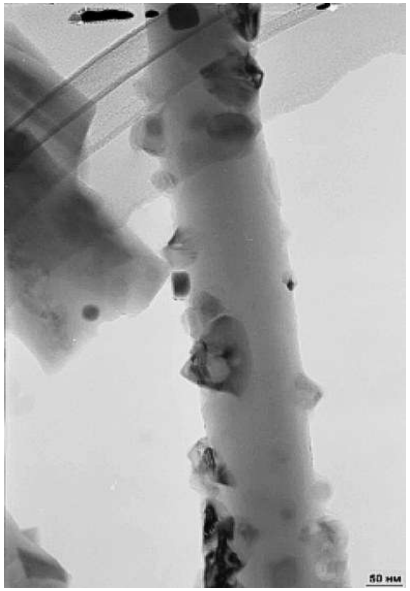
J. Mater. Chem., 2002, **12**, 361–365

Particles and fibers for particulate Si_3N_4 – TiN ceramic nanocomposite



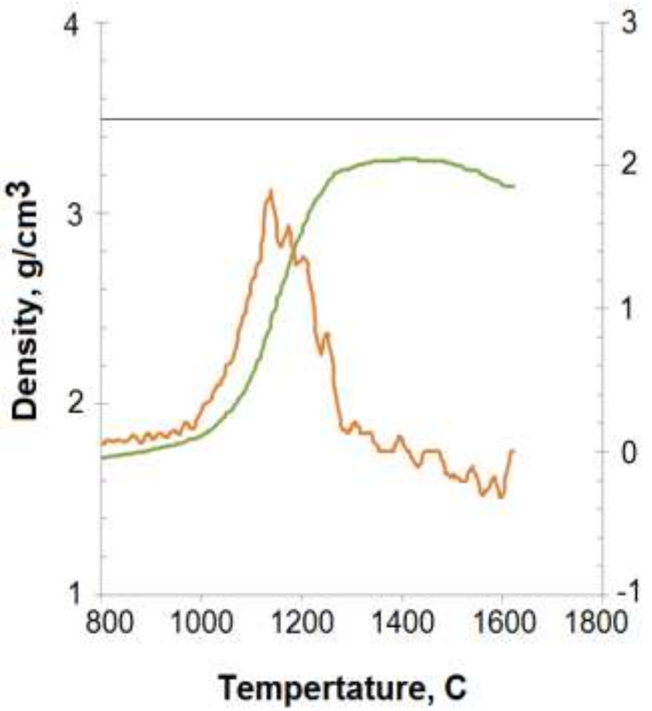


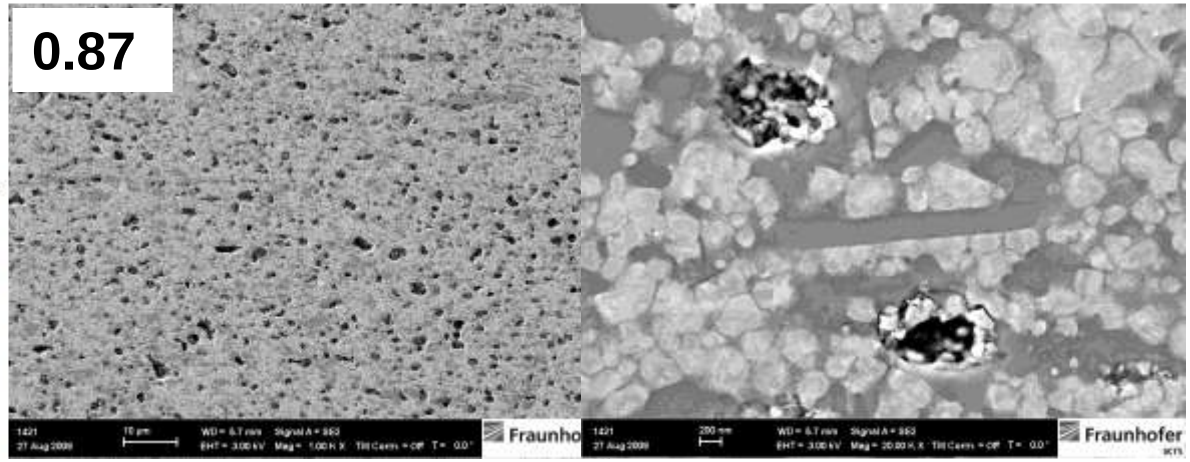




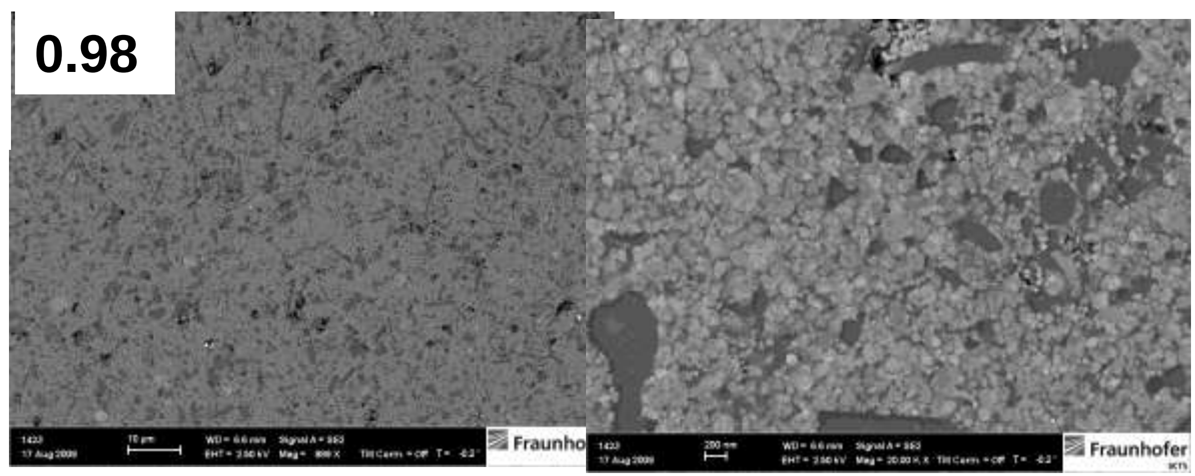
Nanopowder/ composition	Company	$d_{aver.}$, nm	Specific surface, m^2/g	[O], wt.%
TiN	H C Stark	15	25	1.2
Si_3N_4 (6wt.%Y_2O_3 - 5wt%Al_2O_3)	PCT ltd. Latvia	33	30	1.6
w-Si_3N_4 (nanowhiskers)	Nanoamor inc.	d=30-70 l= 300-800	103	<1

SPS of nanocomposite 66TiN-17p-Si_3N_4 –17w-Si_3N_4





Formation of porosity on overheating above 1600 C



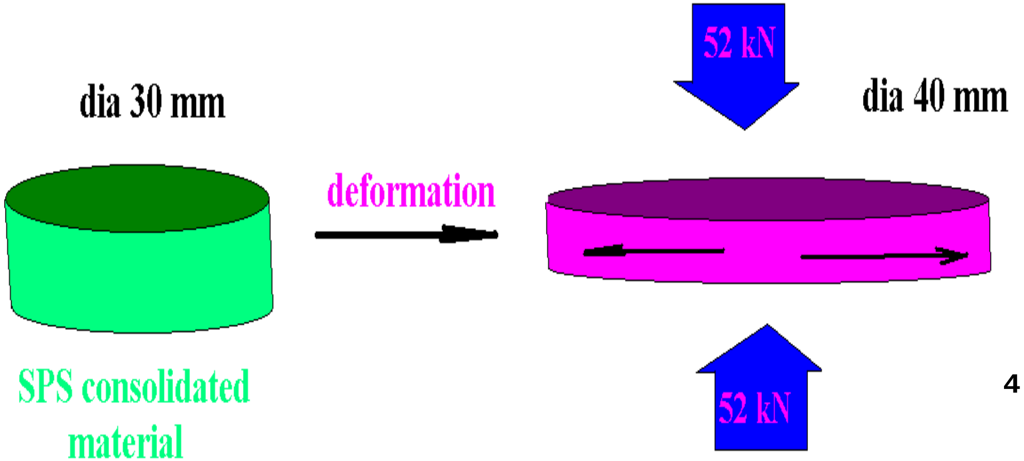
Maximum density at 1450 C, α-Si3N4-TiN

50 MPa,

200 degr/min

1700 C for 1 min

Superplastic deformation of Si3N4 – based ceramics Sinterforging at 1450-1600 C

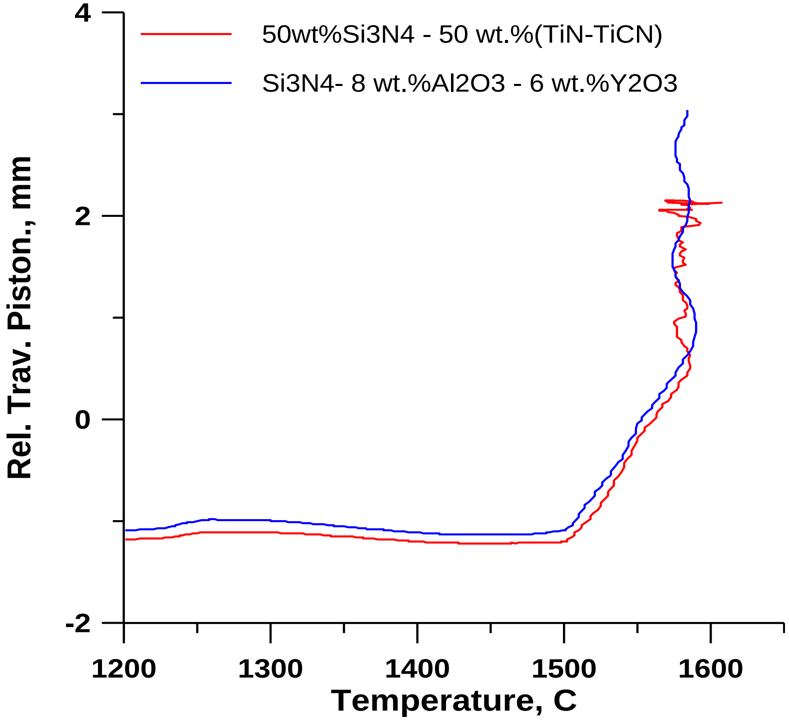


Strain rates for SPS at 1500 ^{0}C:

50TiN-50Si_3N_4 - 1.6x10^{-3}, 1/s

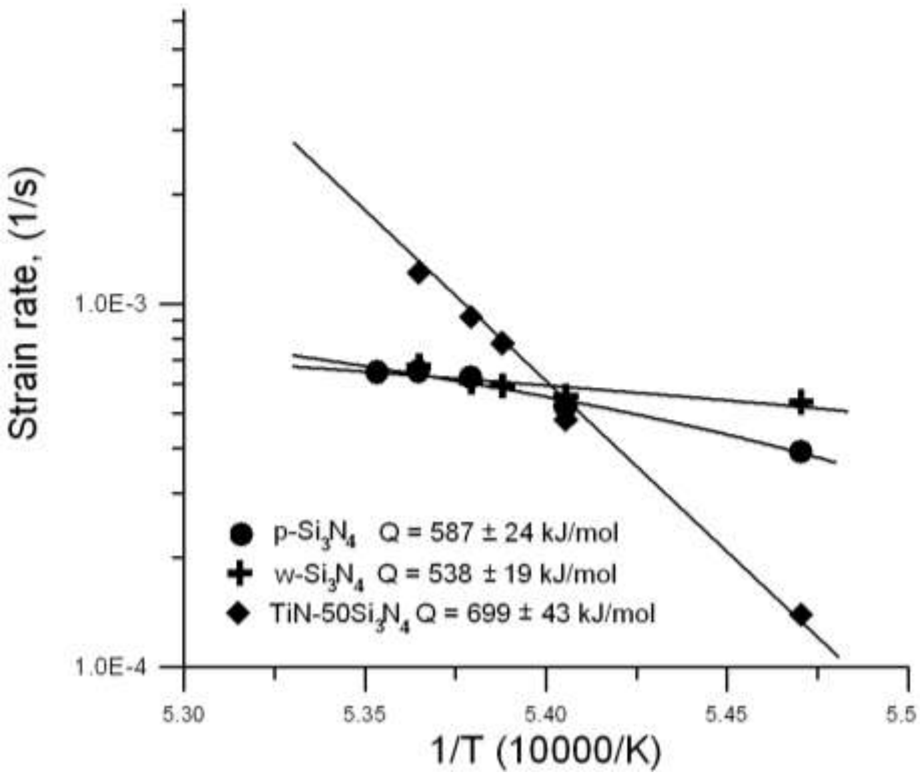
w-Si_3N_4 - 4.6x10^{-3}, 1/s

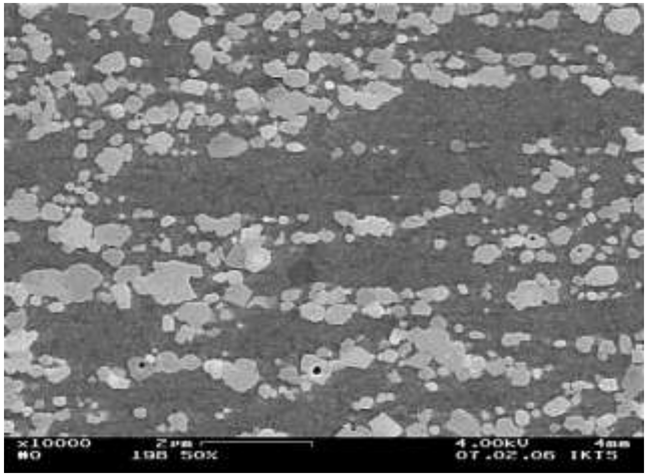
p-Si_3N_4 - 5.4x10^{-3}

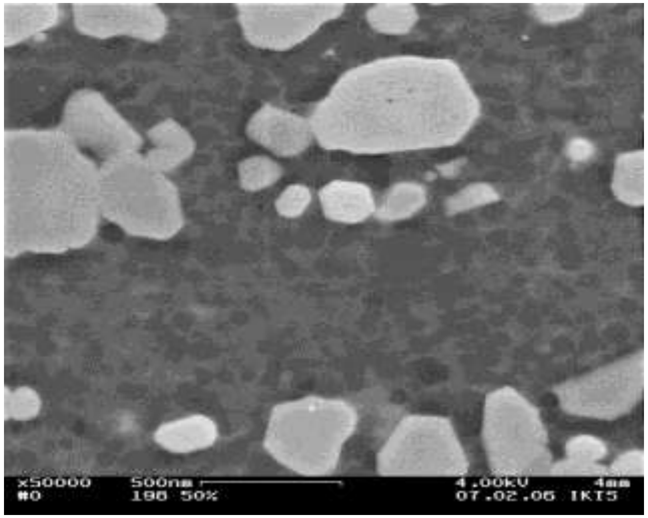


SPS-enhanced sinterforging for net-shaping of TiN-Si3N4 composite

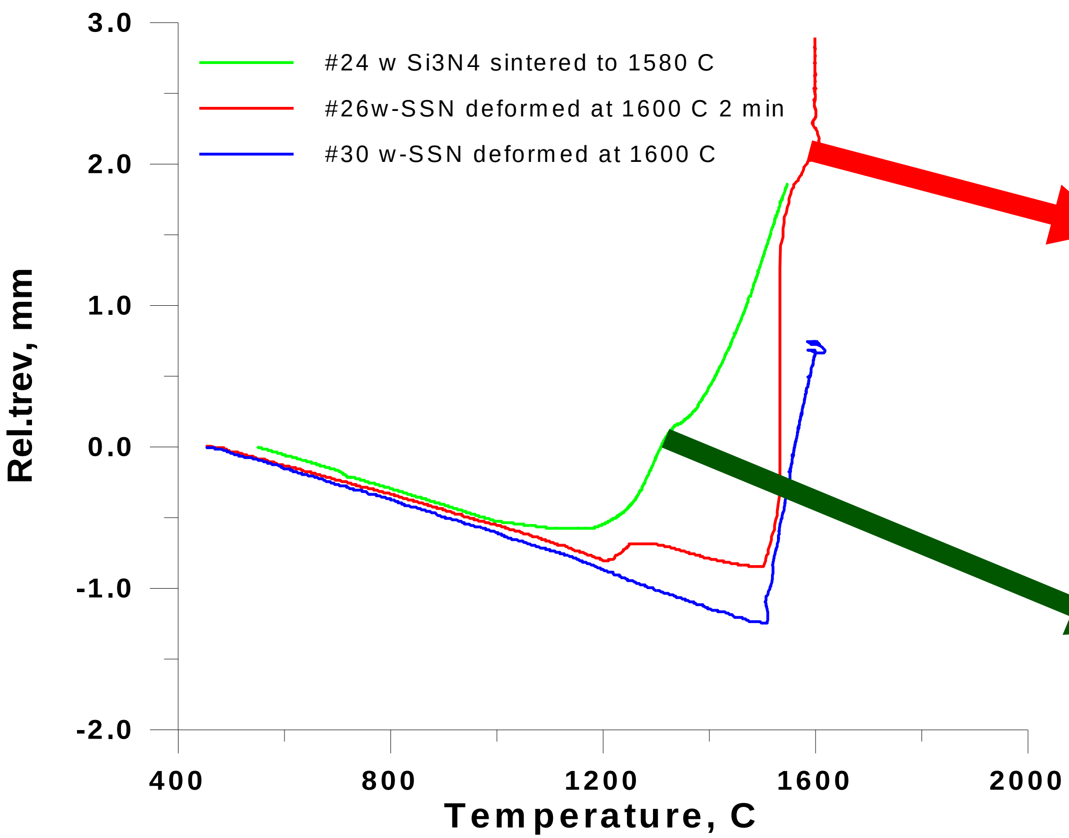
$$\dot{\varepsilon} = \frac{A\sigma^{n}}{d^{p}} \exp\left(-\frac{Q}{RT}\right)$$

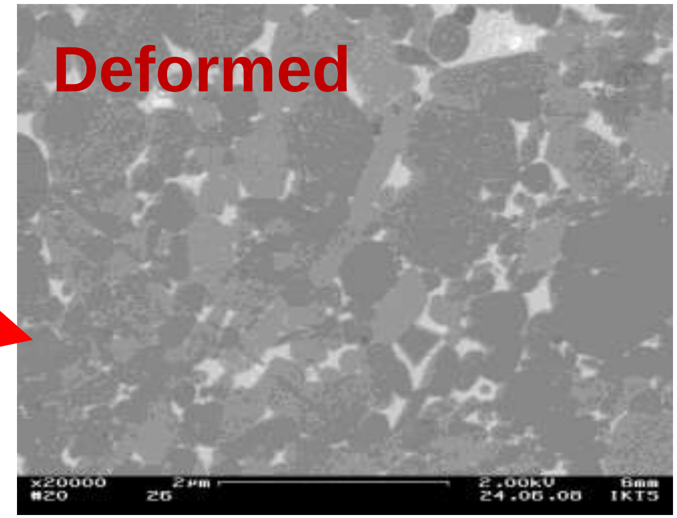




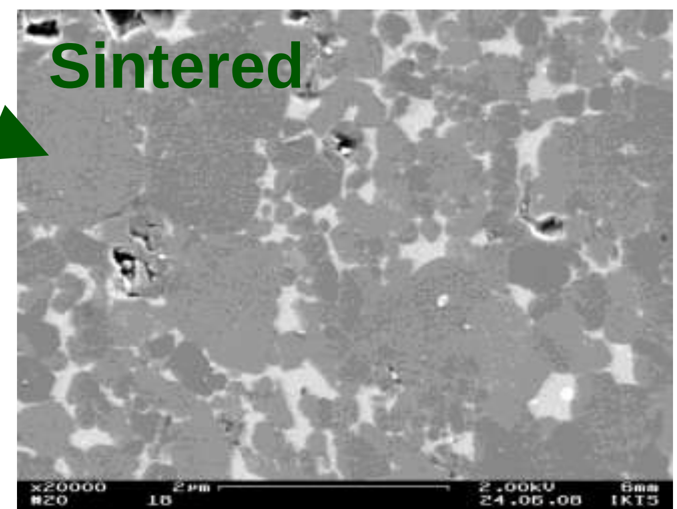


SPS-enhanced sinterforging for net-shaping of Si_3N_4





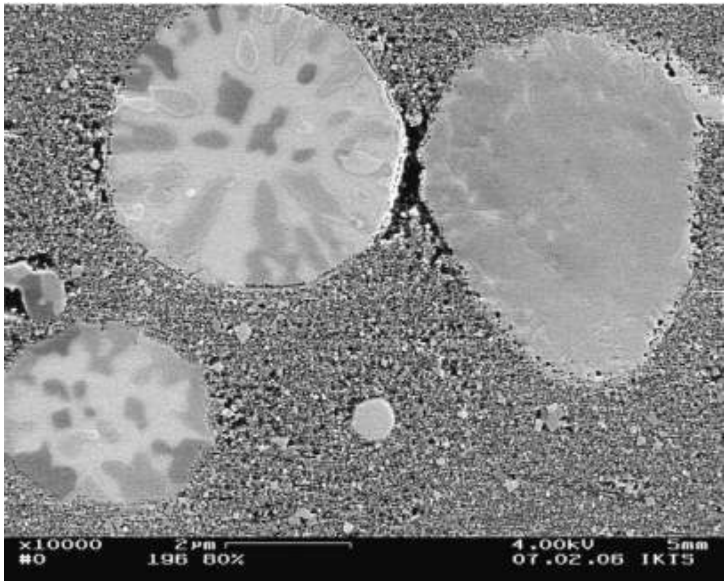
Poreless

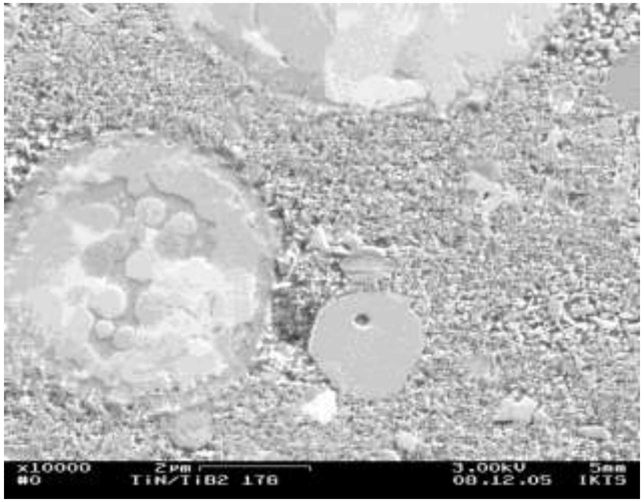


7% porosity

Texture has not been found

Spherical inclusions formed at SPS of nanopowders TiCN, $TiN\text{-}TiB_2$, $TiN\text{-}TiCN\text{-}Si_3N_4$ – the result of multiple internal discharges of huge electric capacity ?

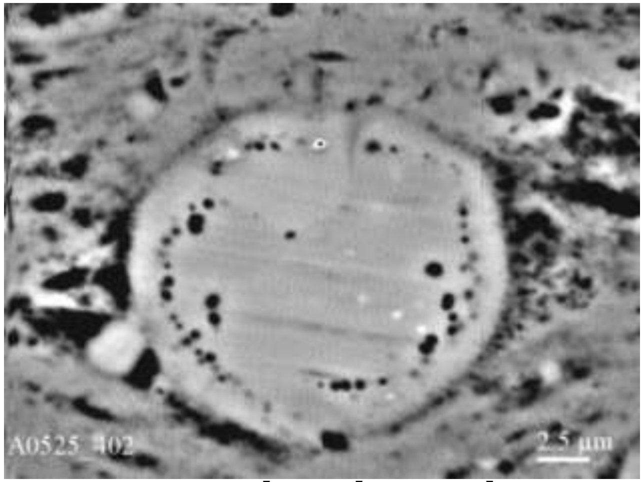




80 wt.% TiN - 20 wt.% TiB_2

Droplets include both conductor and isolator phases

Several agglomerates form porous spherical inclusions inside the ceramic matrix when the total porosity is above 40%

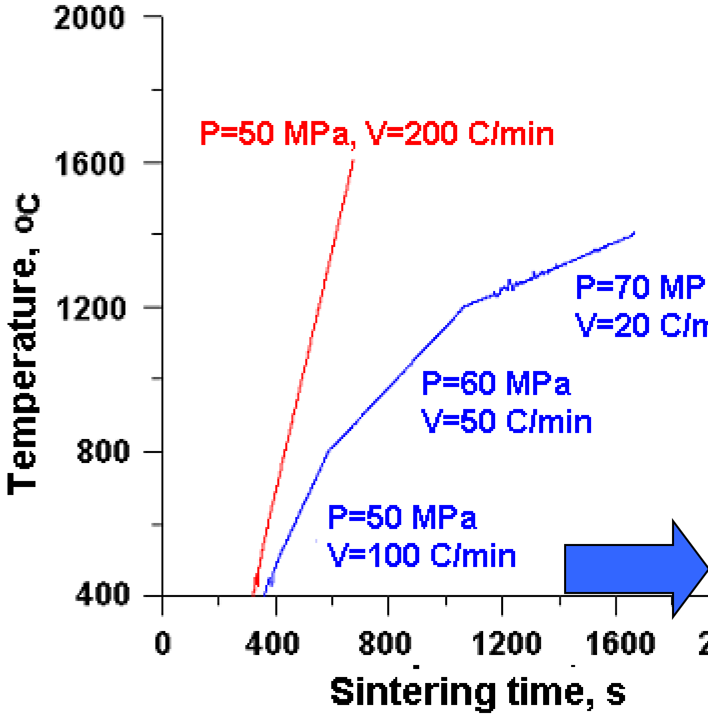


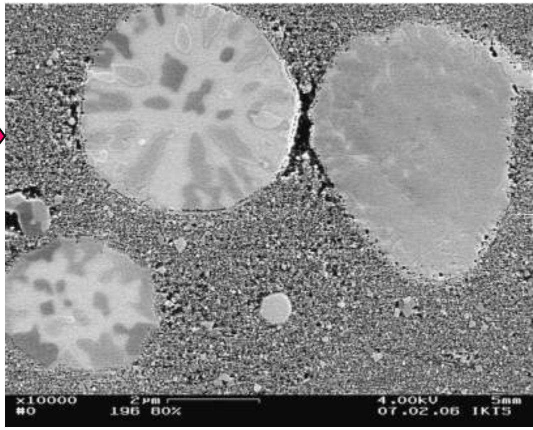
$TiN\text{-}TiCN\text{-}Si_3N_4$

ISS Bukovel-2012

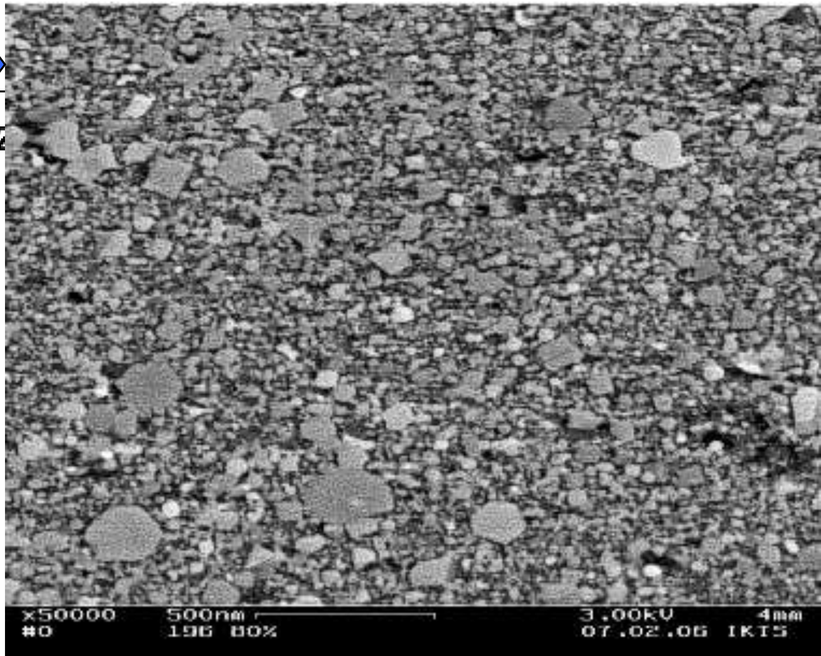
Consolidation of nanopowders TiCN, TiN-TiCN-Si_3N_4, TiN-TiB_2 in the SPS process and schedule optimization.

Relative density of sintered composites:
0.98-0.99 for TiN-TiCN-Si_3N_4
0.93-0.96 for TiN - TiB_2.





Electric discharge spots



Variable pressure and heating rate gives much more uniform structure and density ~99%

This is the first attempt to marry SPS and RCS

Examples of nanoceramics as cutting tools

Material	Hv, GPa	K_{Ic}, MPa $m^{1/2}$	Density, g/cm^3
WC-Co	23-24	>7	15.63
Al_2O_3-diamond	25-30	>3.5	3.8
TiN-25%Si_3N_4	23-24	> 6.5	4.4
TiN-25%Si_3N_4 deformed	23-24	> 7.3	4.4
TiN-25%Si_3N_4 deformed and annealed	22-23	> 8.0	4.4

WC-Co (Inframat), TiN-IPMS

Reaction SPS in the system TiN-TiB2

Thermal effects of reactions (T=298 K)

№	Reaction	Q_1, kJ/mol	Q_2, kJ/g
1.	$TiH_2 + 2/3BN = 2/3TiN + 1/3TiB_2 + H_2\uparrow$	4,58	0,07
2.	$TiH_2 + 2B = TiB_2 + H_2\uparrow$	135,1	1,89
3.	$Ti + 2/3BN = 2/3TiN + 1/3TiB_2$	152,3	2,36
4.	$Ti + 2B = TiB_2$	279,5	4,02

The range of releasing heat for self-propagating high-temperature synthesis (SHS) Q2: 0,42-4,2 kJ/g;

Application of TiH_2 and BN as initial reagents decrease thermal effect – the substantial amount of energy is spent on decomposition of these compounds.

Properties of the initial powders

As initial reagents the follow powders were used: - brittle and well milled cubic TiH_2; hexagonal BN; rhombic B; and nanocrystalline cubic TiN.

Powder	XRD	$S_{spec.}$, m^2/g	$d_{aver.}$, µm	[O], wt%	[Fe], wt%
TiH_2	TiH_2 (cubic)	0,12	12,8	0,13	0,04
BN	BN (hexagonal)	17,8	0,16	6,40	0,03
B	B (rhombic) + B_2O_3+ B (tetragonal) + β-B	5,9	0,43	3,71	0,04
TiN	TiN (cubic)	16,06	0,07	3,68	0,06

The higher value of specific surface area ($S_{spec.}$) and oxygen content have BN, B and TiN powders as compared with TiH_2 powder;

The boron powder contains mainly ultrafine grade of Boron and relatively coarse B_2O_3 phase removable.

Powder mixtures

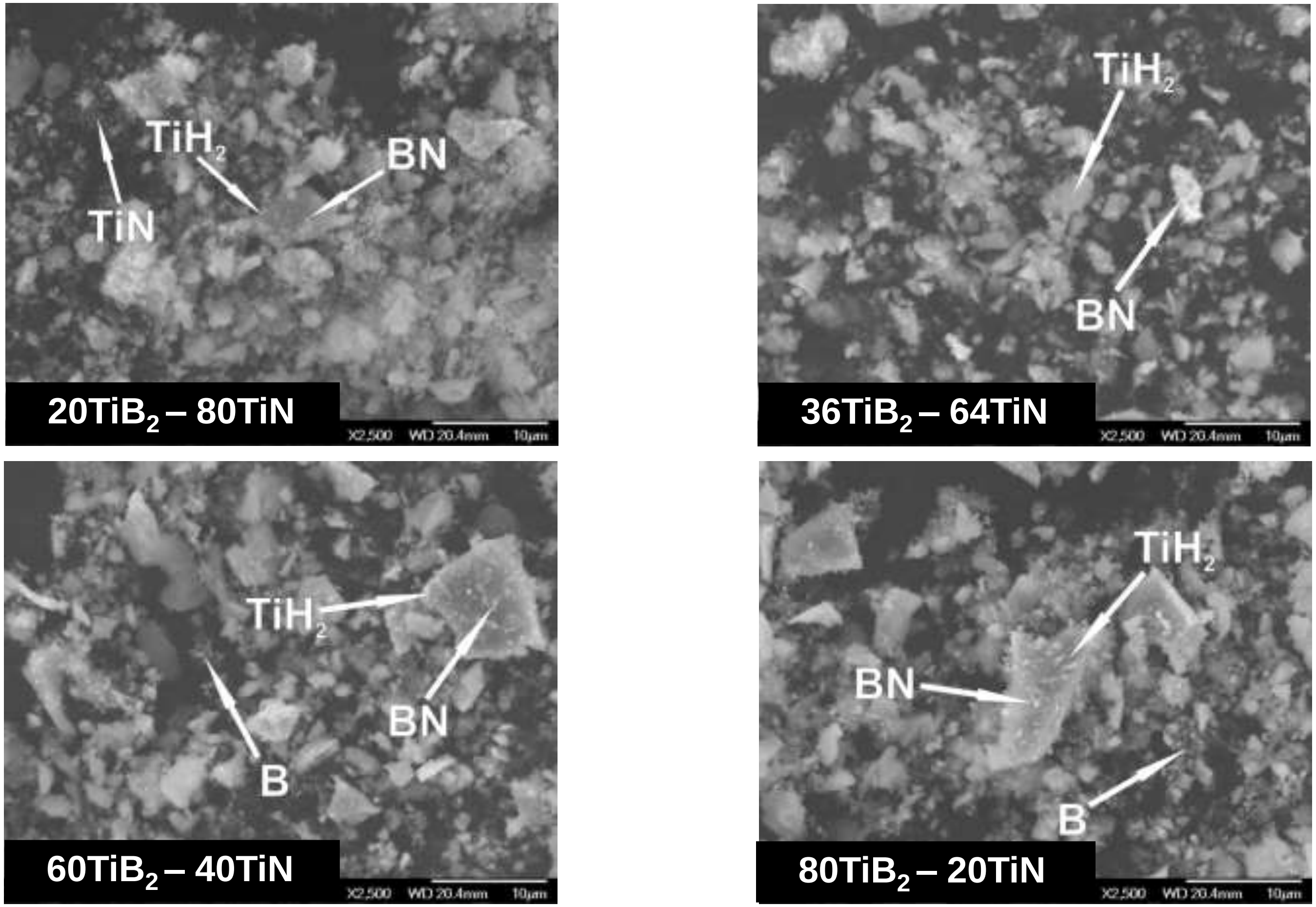
The high energy ball mixing/milling of the initial powder mixtures for 2 h using ethanol and agate balls as milling media were carried out. CR (ball to powders weight ratio) equals to about 1.5 and rotation velocity of the jar – 650 rpm.

Powder mixtures composition, wt%	Composition in sintered composites, wt%	Average particle size, $d_{aver.}$, µm
41,21TiH_2 - 13,09BN - 45,7TiN	20TiB_2 - 80TiN	0,15
75,9TiH_2 - 24,1BN	36TiB_2 - 64TiN	0,41
73,47TiH_2 - 14,93BN - 11,6B	60TiB_2 - 40TiN	0,53
71,56TiH_2 - 7,44BN - 21B	80TiB_2 - 20TiN	0,68

Powder mixtures composition corresponded to 20, 36, 64 and 80 wt% of TiB_2 in sintered ceramic composites;

Calculated from the specific surface area data the average particles size ($d_{aver.}$) varied within 0.15 – 0.68 µm and depended

SEM images of the granulated raw- mixtures



As a result of milling/mixing of the initial powders the formation of relatively coarse (2-4 μm) granules of TiH_2 particles within the shell of ultrafine BN particles has occurred;

The granulated mixture demonstrates higher green and tap density, which makes raw-mixtures more robust

Properties of the TiN/TiB_2 composites SPSed at 1400-1500 °C

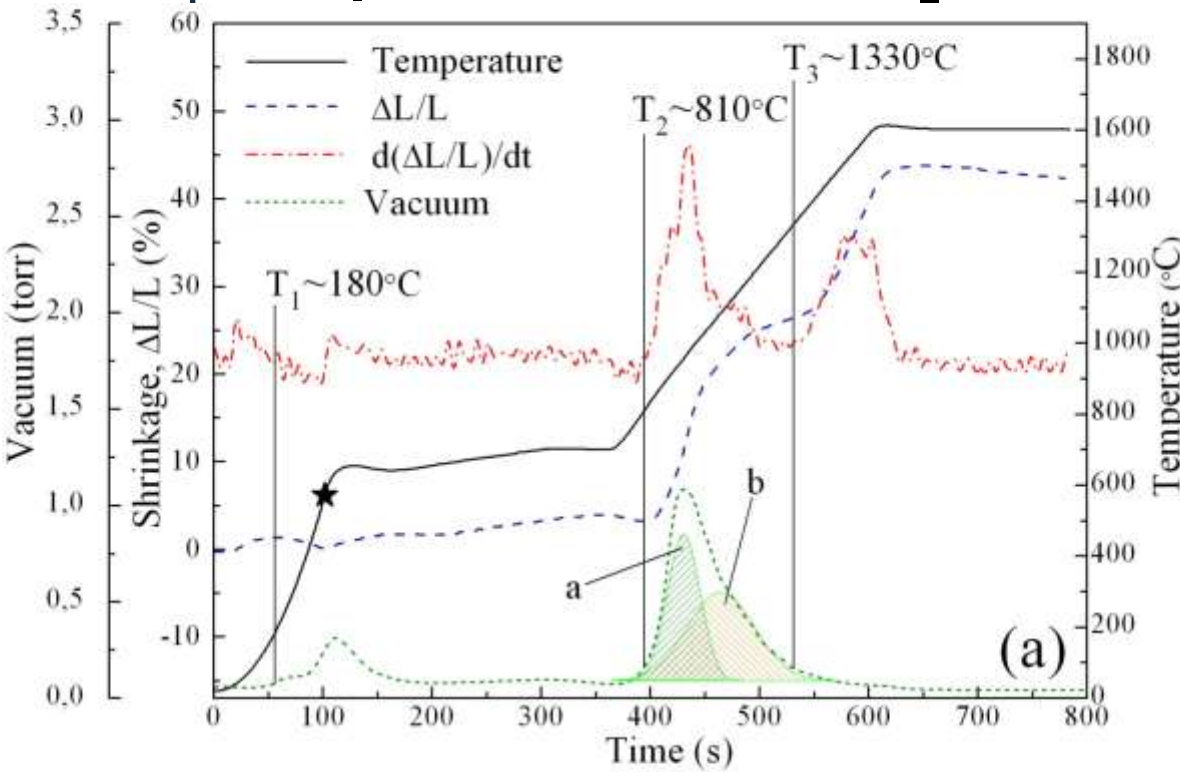
Research	TiB_2, wt %	XRD	Relative density, %	Hardness HV, GPa	Lowest Fracture toughness K_{1C}, $MPa*m^{1/2}$	Sintering temperature t, °C	Sintering time τ, sec.	Specific thermal effect of chemical reaction Q2, kJ/g
1 ERAN	20	$TiN+TiB_2+Ti_{v.small}$	85,2	18,57	2,85	1500	180	0,04
	36	$TiN+TiB_2$	99,4	19,7	7,38	1450	180	0,07
	60	$TiN+TiB_2+Ti_{v.small}$	98,2	25,9	6,80	1480	180	0,76
	80	-	-	-	-	≈900	Destruct. in 12 sec.	1,31
2 Sumitomo	20	$TiN+TiB_2$	91,8	18,18	2,26	1400	670	1,26
	20	$TiN+TiB_2$	94,8	16,2	3,78	1500	480	1,26
	36	$TiN+TiB_2$	84,7	9,2	3,68	1400	480	2,36
	36	$TiN+TiB_2$	95,9	20,6	2,29	1500	480	2,36
	60	$TiN+TiB_2$	80,2	6,2	3,07	1400	600	3,06
	80	$TiN+TiB_2$	63,7	3,6	absence of cracks	1400	600	3,54

The high heating rate (1680-2520 °C/min) and simultaneous release of hydrogen, reaction and initial stage of consolidation (Research 1) leads to increasing mechanical properties with increasing boron content in initial powder mixtures and consequently TiB_2 in sintered samples;

Relatively low heating rate (120-300°C/min) (Research 2) leads to formation of structural skeleton preventing shrinkage on the early stage sintering. It results in decreasing of composite properties, mostly density and density related mechanical properties.

Staging of reactive SPS for TiN-TiB_2 composites

Composition: 36 wt% TiB_2 – TiN ; Heating rate – 225



TiH$_2$ dehydrogenation is completed at a temperature of about 900-960 °C. The dehydrogenation peak coincides with the greater shrinkage rate in the <u>2nd Stage</u> and, thus, with the highest reaction rate;

Peak *b* (second drop in the vacuum level) is evidence of the formation of secondary hydrogen.

<u>1st Stage</u> is start of TiH_2 dehydrogenation at T_1~180°C, $TiH_2 \rightarrow TiH_{2-x} + xH\uparrow$;

<u>2nd Stage</u> involves chemical reaction in the system during the most intensive dehydrogenation process,

$3TiH_2 + 2BN \rightarrow 2TiN + TiB_2 + 3H_2$ (6H)↑ $2TiH_2 + BN + B \rightarrow TiN + TiB_2 + 2H_2$ (4H)↑

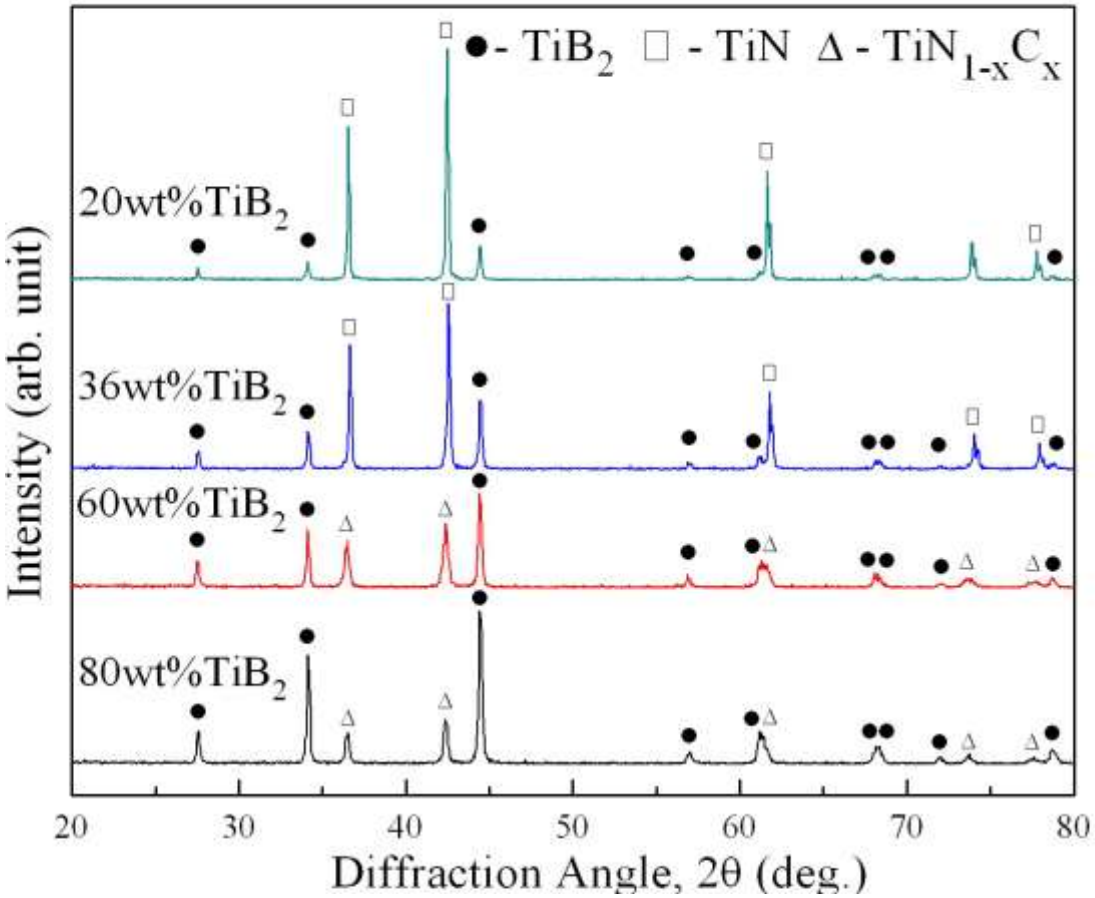
$2BN + 6H \rightarrow B_2H_6 + 2N\uparrow$
$Ti + N \rightarrow TiN$
$B_2H_6 \rightarrow 2B + 3H_2$ (6H)↑
$Ti + 2B \rightarrow TiB_2$

The possibility of a simultaneous solid-state reaction cannot be excluded;

<u>3rd Stage</u> is direct sintering of the synthesized TiN and TiB_2 components;

XRD patterns of the sintered samples

XRD patterns of ceramic composites consolidated via reactive SPS with a heating rate of 225 °C/min as a function of TiB_2



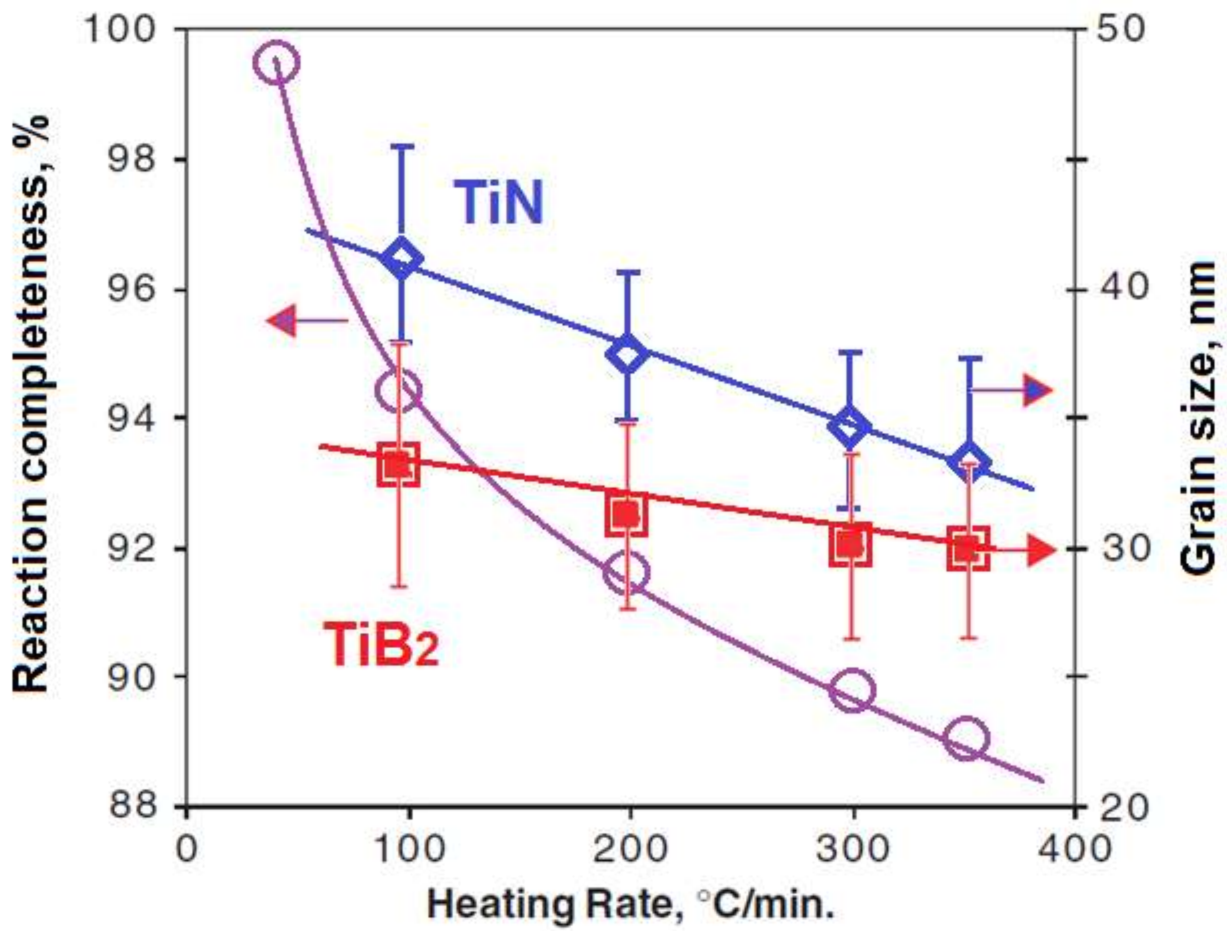
Heating rate of 112,5 ºC/min – formation of TiN and TiB_2 phases;

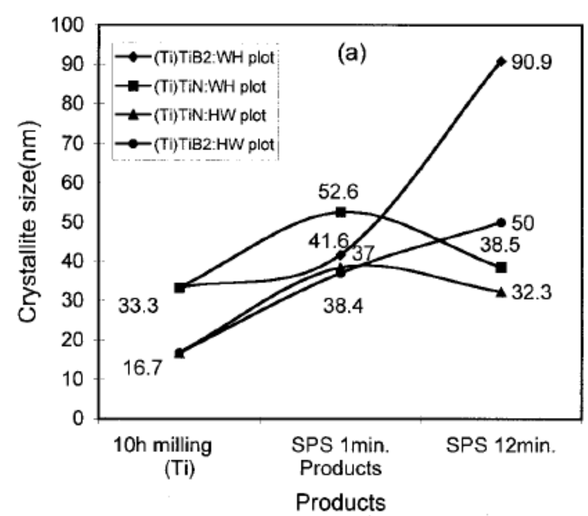
Heating rate of 225 ºC/min – formation of TiN and TiB_2 phases (20 and 36 wt% TiB_2) ; $TiN_{1-x}C_x$ phases (x=0,1-0,3) and TiB_2 (60 and 80 wt% TiB_2);

Heating rate of 300 ºC/min – formation of $TiN_{1-x}C_x$ and TiB_2 phases.

XRD patterns of the as -reacted samples

XRD patterns allows calculating grain sizes of TiN and TiB2 versus heating rate





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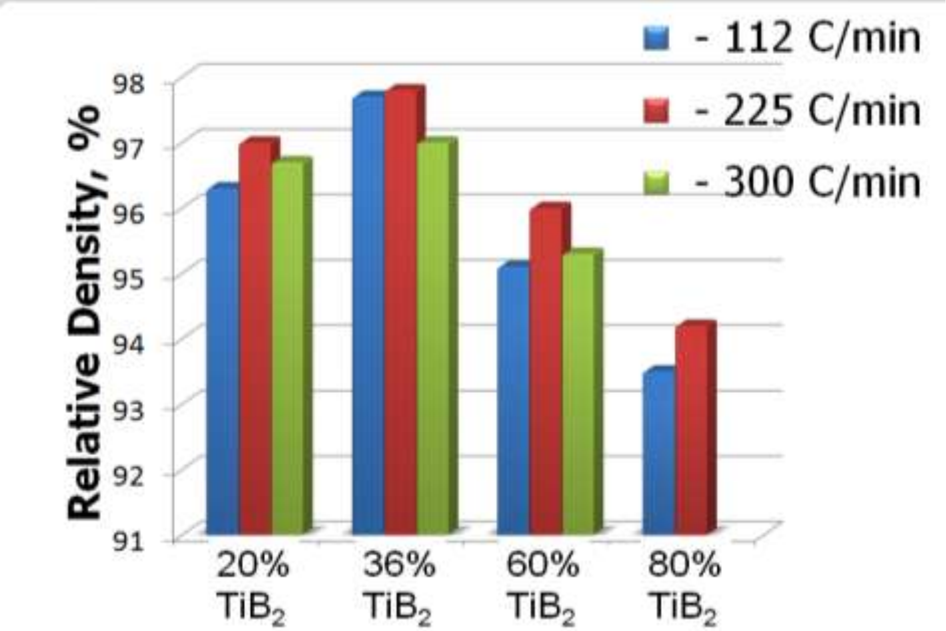
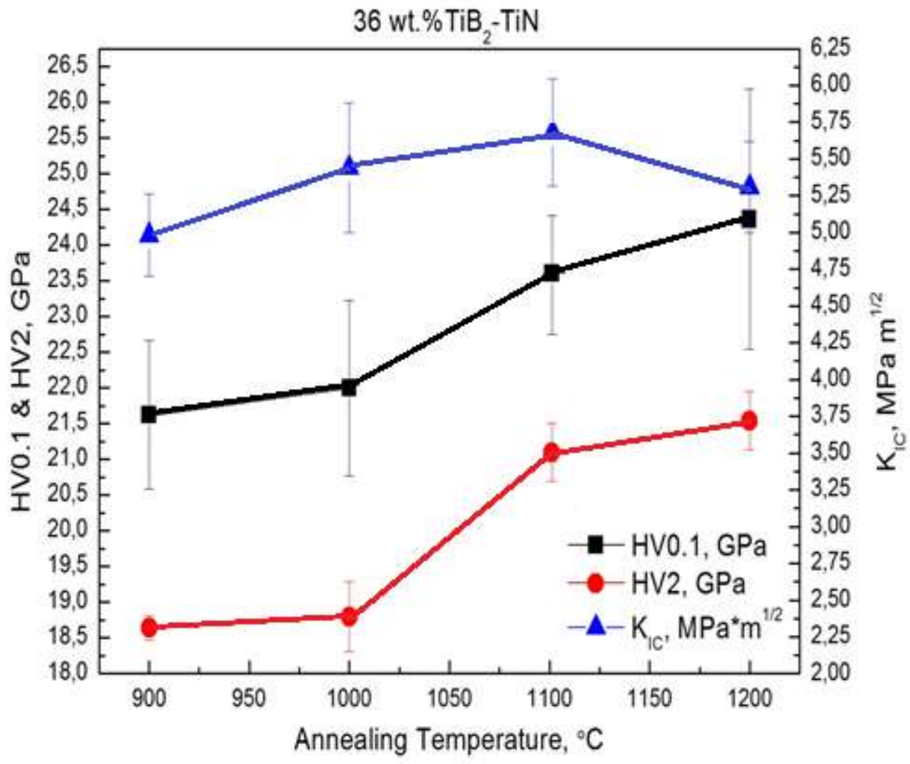
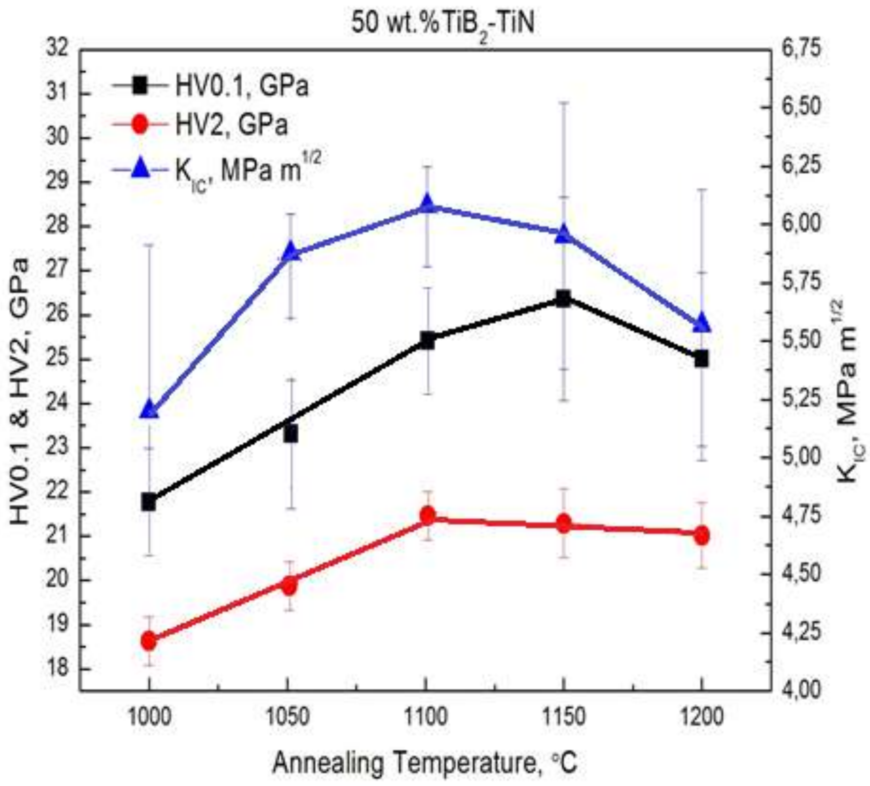
Properties of the TiN/TiB_2 composites SPSed in FCT HPD25

Composition, wt%	Heating rate, °C/min	Relative density, ρ, %	HV, GPa		K_{1c}, $MPa \times m^{1/2}$
			Load, P= 0.1 kgf	Load, P= 2 kgf	
20 TiB_2- 80 TiN	112.5 225 300	96.3 97.0 96.7	18.9 (+/-1.0) 19.5 (+/-0.6) 21.3 (+/-1.1)	17.7 (+/-0.4) 18.0 (+/-0.6) 18.4 (+/-0.6)	4.06 (+/-0.2) 4.07 (+/-0.1) 6.16 (+/-0.7)
36 TiB_2- 64 TiN	112.5 225 300	97.7 97.8 97.0	21.0 (+/-1.0) 20.4 (+/-1.7) 21.5 (+/-0.9)	19.8 (+/-0.3) 20.3 (+/-0.6) 19.8 (+/-0.3)	4.37 (+/-0.1) 5.05 (+/-0.2) 4.80 (+/-0.1)
60 TiB_2- 40 TiN	112.5 225 300	95.1 96.0 95.3	22.0 (+/-1.8) 21.5 (+/-3.7) 22.7 (+/-2.8)	20.6 (+/-0.6) 19.5 (+/-0.6) 19.2 (+/-1.8)	4.74 (+/-0.2) 4.59 (+/-0.2) 5.04 (+/-0.4)
80 TiB_2- 20 TiN	112.5 225 300	93.5 94.2 Destr. at 865 ºC	24.7 (+/-4.4) 16.5 (+/-3.2) -	24.6 (+/-3.3) 15.9 (+/-0.7) -	5.17 (+/-0.4) 6.46 (+/-0.9) -



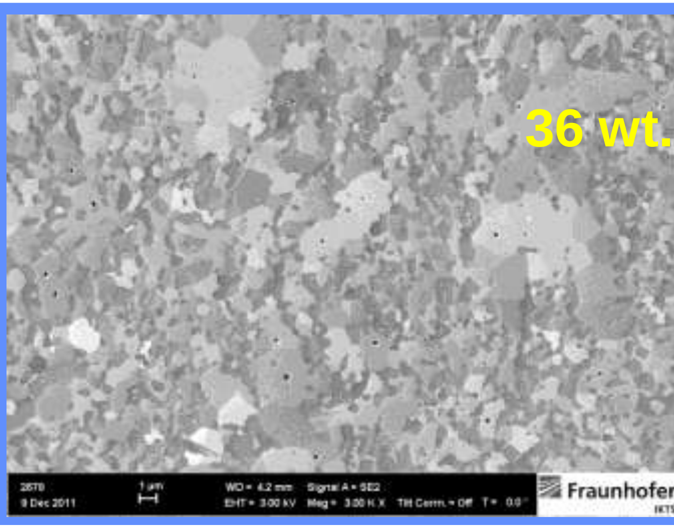
Properties of the TiN/TiB_2 composites SPSed at 1600 °C

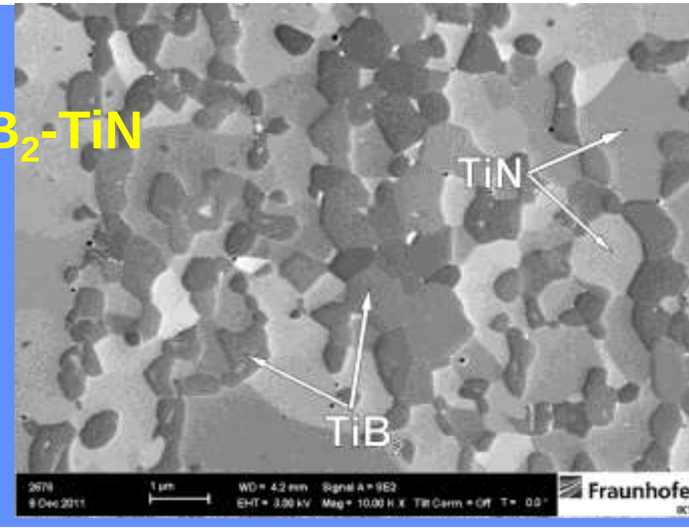




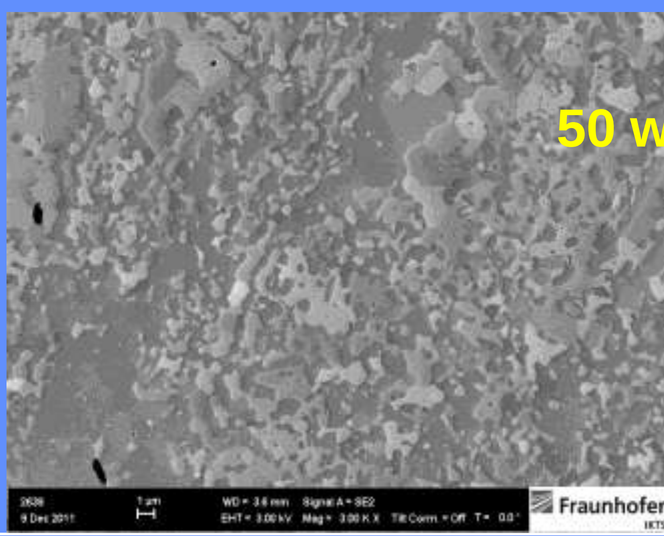
Heat treatment allows minimizing thermal stresses, equilibrate grain boundaries and improve mechanical properties.

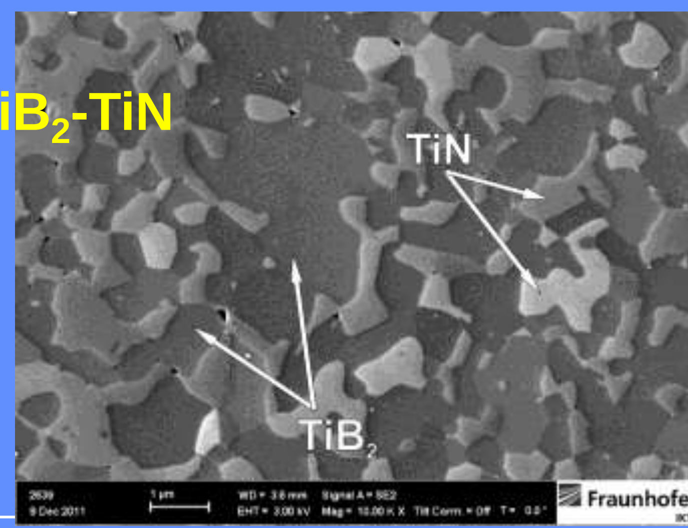
SEM images of the SPSed ceramic composites





36 wt.% TiB_2-TiN





50 wt.% TiB_2-TiN

Conclusions:

FAST/SPS allows consolidation of dense nanograin materials with various chemical bonding for short period of time

It differs from conventional sintering and hot pressing because the electric field allows much faster heat and mass transfer providing much faster shrinkage of both conductors and dielectrics

Process allows Sinterforging treatment and netshaping of high-melting nanomaterials because of their high-temperature structural superplasticity

Ceramics sintered under FAST/SPS conditions requires heat treatment (annealing) to remove residual stresses and equilibrate grain boundaries.

Acknowledgements:

Dr. Zgalat-Lozynskyy, Dr. Petukhov, Mr. Khobta, Mr. Kolesnichenko - all members of my team at IPMS

Dr. Herrmann and Dr. Raethel - both from IKTS

Dr. Sakka and Dr. Vasylkiv – both from NIMS

THANK YOU FOR ATTENTION

Challenges for the particulate nanomaterials

Two alternative approaches are valid to get consolidated 3D nanomaterials:

- **bottom-up assembling from preliminary prepared nanoparticles using slow colloidal processes followed by rapid sintering techniques**
- **top-down refining the microstructure using intermediate reaction followed by rapid sintering techniques in one process**

Triune task for the nanomaterials manufacturing by powder technology

- **The specifically formulated homogeneous nanosized powders with given «chemistry» of a surface layers are required:**

  -- structure of agglomerates must be controlled directly during synthesis or additionally afterwards;

  -- synthesis of in-situ composite nanopowders (the «core-shell» type) is preferable;

  -- problem of surface protection for particle handling and storage have to be solved;

- **Combination of powder consolidation methods (including cold and hot consolidation) are to be developed to retain nanosize grains and provide perfect grain boundaries / interfaces in bulk nanomaterials;**
- **The size effect achieved in properties crowns all efforts;**

Глобальный рынок нано- композитов

• Глобальное потребление нанокомпозитов измеряется 67,685 тонн или $467 млн. в 2008. До 2014, рынок возрастет до 214,081 тонн и $1.38 млрд., (CAGR 27.1%).

• Общий рынок нанокомпозитов с керамической матрицей составлял 10,662 метрических тонн или $49.8 млн. в 2008. Увеличится до 17,388 тонн или $145.2 млн. в 2014 CAGR12.5%.