Chemical aspects of Spark Plasma Sintering: possibilities and challenges of microstructure control of the synthesized materials

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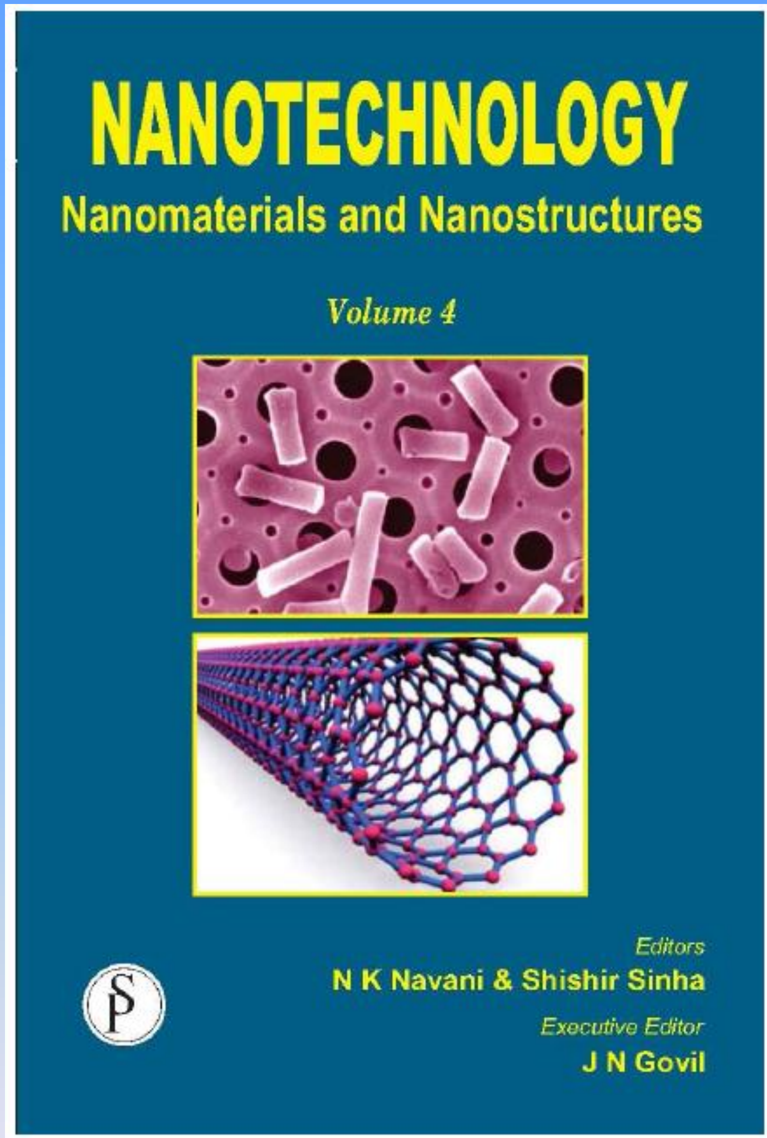

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Reactive Spark Plasma Sintering for the Production of Nanostructured Materials

DINA V. DUDINA[1]* AND AMIYA K. MUKHERJEE[2]

ABSTRACT

Spark Plasma Sintering (SPS) has attracted a lot of attention from researchers and engineers in the past two decades as a promising method of fast and effective densification of metallic and ceramic materials. Based on the simultaneous application of electric current and uniaxial pressure to the sample, SPS offers high heating rates and sintering within shorter times and at lower temperatures than in conventional methods thereby minimizing grain growth and making it possible to produce nanostructured bulk materials from nanopowders. Chemical reactions between powder materials can be easily initiated in the SPS, which opens up a possibility of combining a synthesis and a sintering step and presents a useful design tool of composite microstructures. Challenges of reactive sintering are related to additional factors that come into play with the occurrence of chemical transformations, such as uniformity of distribution of the reactants in the mixture, heat release during exothermic reactions, specific volume change, presence of reaction by-products or remaining reactants due to incomplete reactions. Is SPS as powerful in making nanostructured materials by chemical reactions as it is in sintering non-reacting nanopowders? Is it always necessary to have nanosized reactants to produce nanostructured products and do the former guarantee the latter? This chapter is aimed at answering these questions and analyzing the factors influencing the microstructure development in the powder mixtures reacting in the SPS and conditions favoring densification and completeness of the reaction.

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Introductory remarks

A great variety of materials – ceramics, composites, nanostructured materials, porous materials – have been synthesized using SPS.

Is it possible to conclude from the experimental data whether the synthesis in the SPS can be performed in a controlled manner?
If yes, what are the general approaches?

Based on our research results and literature overview, we have made an attempt to highlight the features of the SPS as a synthesis method and analyze possible microstructure control schemes of the reaction products.

Outline

1. **Reactive SPS: process features and reaction types**
2. **What influences the microstructure of the reaction products?**

- structure of powder precursors
- selected SPS regimes

3. Challenges of producing dense fine-grained materials

4. Undesirable chemical reactions in the SPS

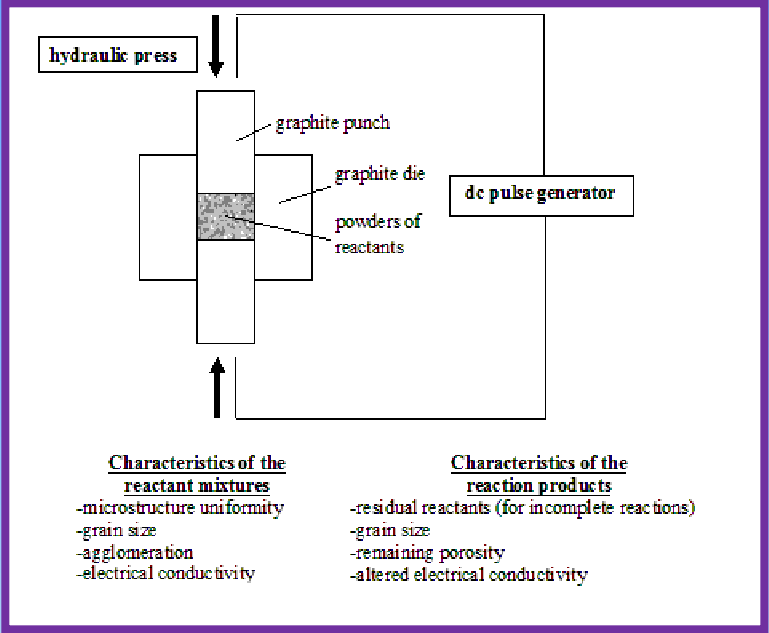
5. Materials with valuable properties obtained by reactive SPS: examples

6. Future uses of reactive SPS for the synthesis and design of novel materials

Reactive SPS: process features and reaction types

SPS-dies as chemical reactors: inherent advantages

- high-temperature synthesis under protective conditions of dynamic vacuum
- rapid heating and cooling, metastable crystalline structures and microstructures
- enhanced reactivity for certain systems, lower reaction onset temperatures
- reducing atmosphere, reduction of contaminating oxides, in situ reduction to form the targeted oxygen-deficient phases
- powder or consolidated products of synthesis possible



Types of chemical reactions possible in the SPS

- Targeted synthesis of new compounds from the reactant mixtures
- Decomposition reactions
- Reduction of oxides (in the reducing environment of the SPS-chamber)
- Interfacial reactions between the phases in composites

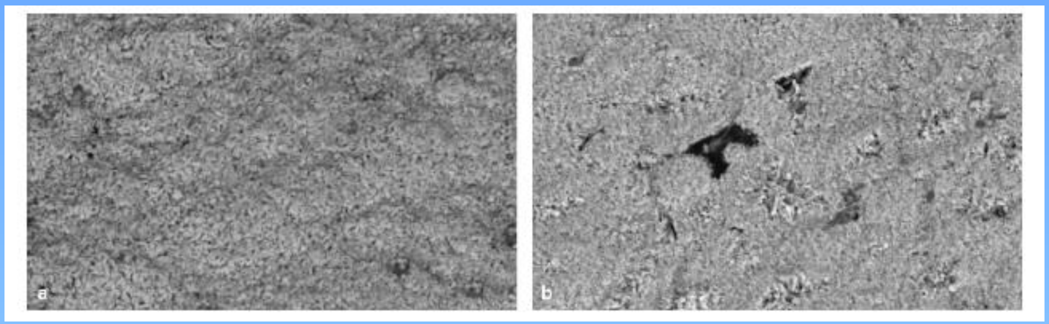
D. V. Dudina, A. K. Mukherjee. In: Nanotechnology, vol.4: Nanomaterials and Nanostructures, Studium Press LLC, USA, 2013, pp. 237-264.
R. Orrù, R. Licheri, A. M. Locci, A. Cincotti, G. Cao. Mater. Sci. Eng. R 63 (2009) 127–287.

Reactive SPS: process features and reaction types

Characteristics of reactive sintering	The consequences for the SPS-process/how the issue is dealt with
1. The degree of distribution uniformity of the reactants in the mixture	**Non-uniform distribution of zones of high electrical conductivity can result in high-temperature-induced processes occurring locally (reaction, melting, phase redistribution, decomposition)**
2. Initiation of the reaction locally in certain preferred zones	**The reaction initiates in the vicinity of zones of higher electrical conductivity, additives of high electric conductivity can be used to initiate the reaction**
3. Heat release in exothermic reactions	**The programmed temperature schedule can be followed**
4. Porosity generated due to a reduction in the specific volume as a result of the reaction	**If SPS is performed under pressure, the porosity can be eliminated**
5. The formation of reaction by-products	**Gaseous by-products are easily removed under dynamic vacuum**

Reactive SPS: process features and reaction types

The reaction initiates in the vicinity of zones of higher electrical conductivity

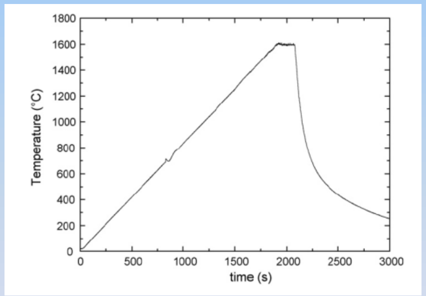


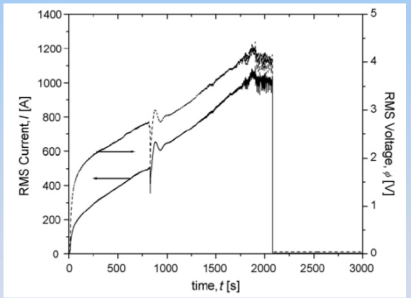
Mg additions to locally increase the electrical conductivity of the Ti-B mixture

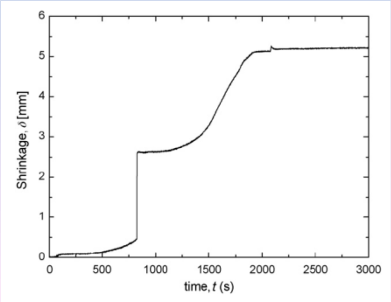
$Ti+2B \rightarrow TiB_2$ in the presence of Mg additions $Ti+2B \rightarrow TiB_2$

D. Salamon, M. Eriksson, M. Nygren, Z. Shen, J. Amer. Ceram. Soc. 90 (2007) 3303.

Heat release in exothermic reactions is balanced by the power input according to the programmed temperature schedule

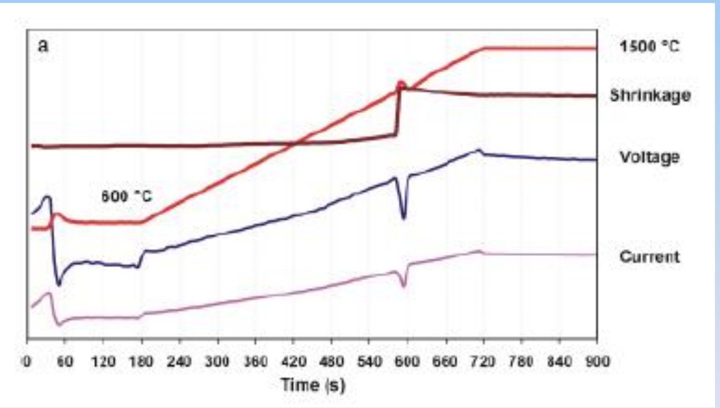






$Re+2B \rightarrow ReB_2$

A. M. Locci, R. Licheri, R. Orrù, G. Cao. Ceram. Inter. 35 (2009) 397.



$Ti+2B \rightarrow TiB_2$ in the presence of Mg additions

D. Salamon, M. Eriksson, M. Nygren, Z. Shen, J. Amer. Ceram. Soc. 90 (2007) 3303.

What influences the microstructure of the reaction products?

Powder precursors

Reactant mixtures prepared by different methods	Possible results of the microstructure development
1. Mixtures of nanopowders	**Nanostructured product if not overheated during SPS**
2. Mechanically milled mixtures	**Nanostructured product if not overheated during SPS**
3. Multicomponent amorphous precursors	**Nanostructured product if not overheated during SPS**
4. Reactant mixtures containing diluents	**A reduced particle size compared to the non-diluted mixtures**
5. Conventional powder mixtures (micron-sized powders)	**Micron-sized product; nano-sized products possible when reaction proceeds through multiple steps**

The microstructure of the precursor is of primary importance.

In order to initiate the reaction at many nucleation sites at the same time, a large number of contact points between the solid reactants should be established.

D. V. Dudina, A. K. Mukherjee. In: Nanotechnology, vol.4: Nanomaterials and Nanostructures, Studium Press LLC, USA, 2013, pp. 237-264.

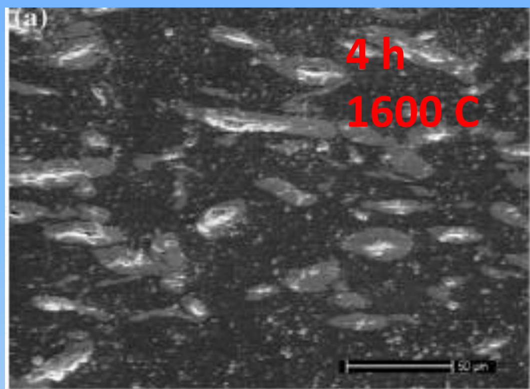
What influences the microstructure of the reaction products?

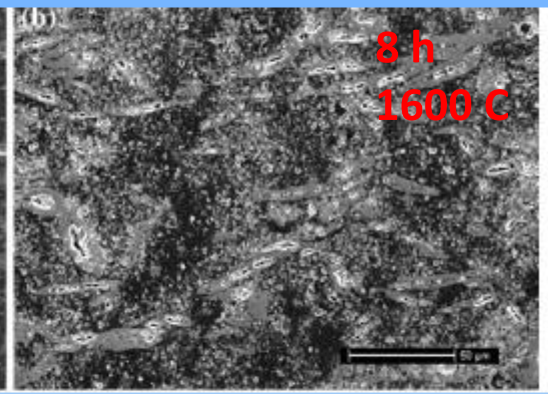
Powder precursors

Mechanical milling: achieving a better mixing uniformity

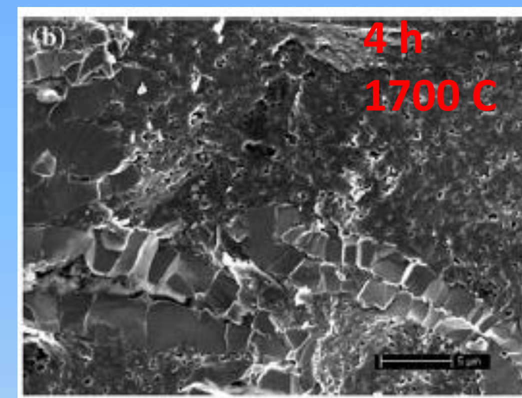
In situ synthesis of 23 vol.% TiB_2 - 77 vol.% B_4C from mechanically milled Ti-B-C mixtures

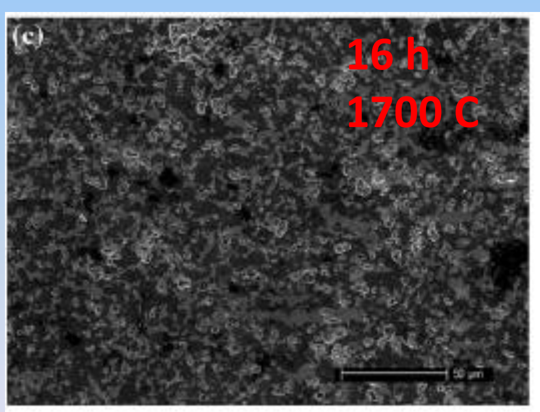
polished





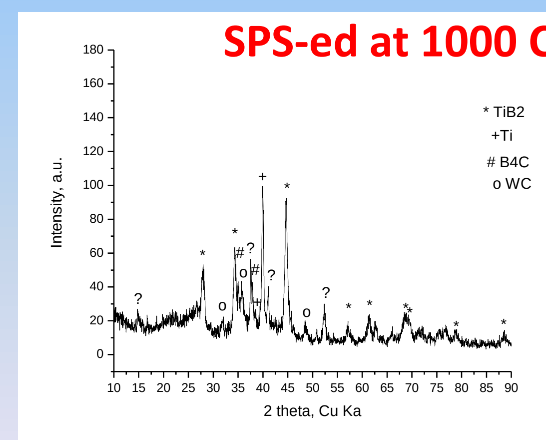
fracture surface





TiB_2 agglomerates: the major part of the total porosity of the composites

Reason: earlier formation of B_4C, which was already quite dense by the moment the reaction between Ti and B was complete, did not allow TiB_2 grains to rearrange and better sinter between themselves.



D. V. Dudina, D. M. Hulbert, D. Jiang, C. Unuvar, S. J. Cytron, and A. K. Mukherjee. J. Mater. Sci. 43 (2008) 3569.

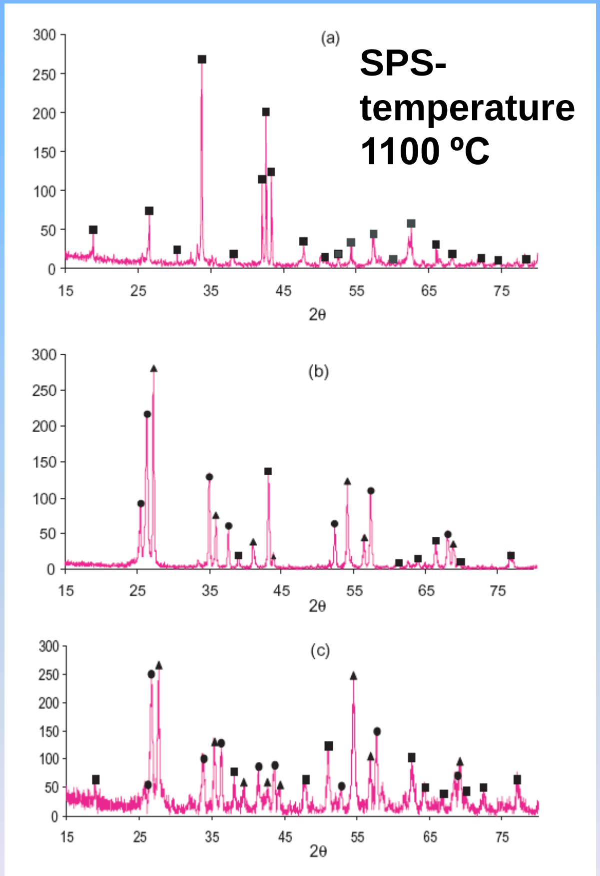
D. M. Hulbert, D. Jiang, D. V. Dudina, A. K. Mukherjee. Intl. J. Refractory Hard Mater. 27 (2009) 367.

What influences the microstructure of the reaction products?

Powder precursors

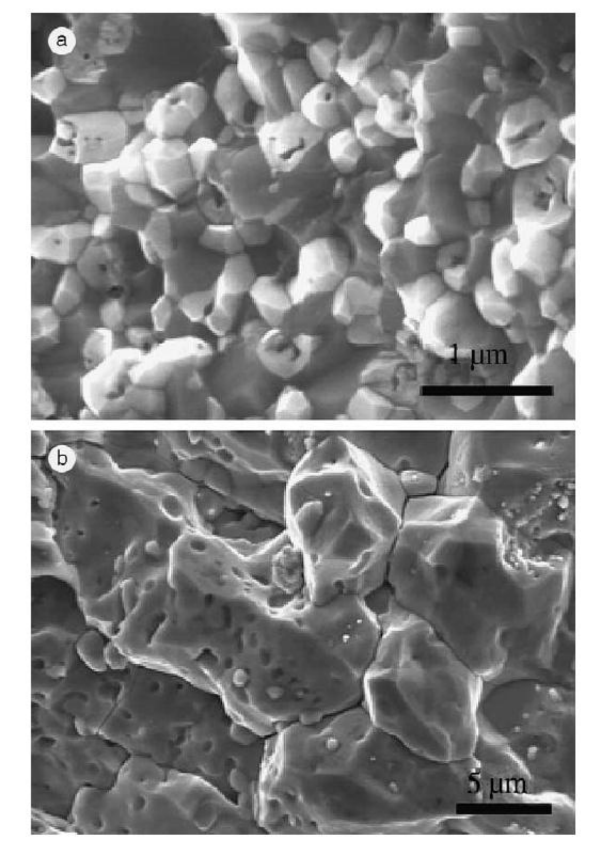
A comparative study: powder precursors prepared by different methods in the synthesis of Al_2TiO_5 from Al_2O_3 and TiO_2

Co-gelified Al_2O_3 and TiO_2 powders: the onset reaction temperature is lower than that for the other two mixtures, the reaction is complete after SPS at 1100°C. The product Al_2TiO_5 has submicron grains.



XRD patterns
a - co-gelified Al_2O_3 and TiO_2
b - mechanical mixtures of Al_2O_3 and TiO_2 individual sol–gel powders
c- powders synthesized by co-precipitation

SEM, fracture surface
a - co-gelified Al_2O_3 and TiO_2 powders
b - powders synthesized by co-precipitation



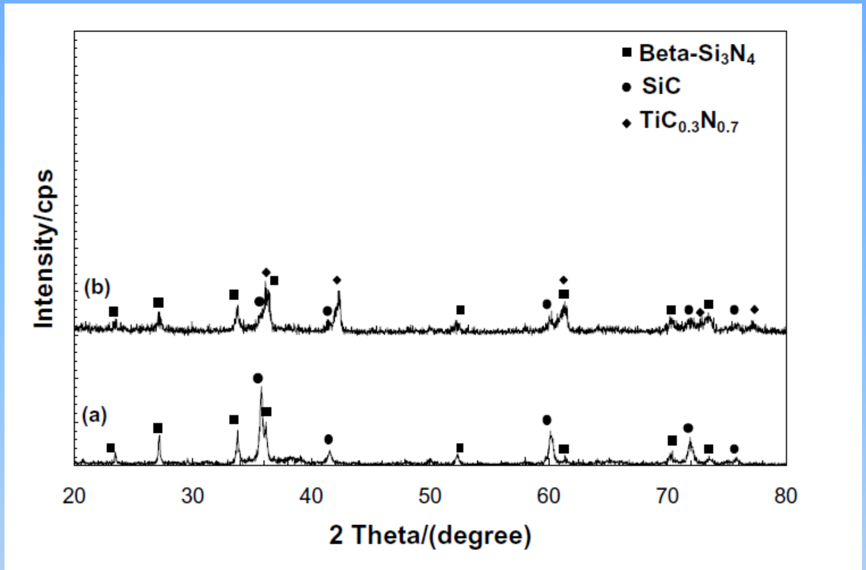
squares-Al_2TiO_5, triangles-TiO_2, circles-Al_2O_3

L. Stanciu, J. R. Groza, L. Stoica, C. Plapcianu. Scripta Mater. 50 (2004) 1259.

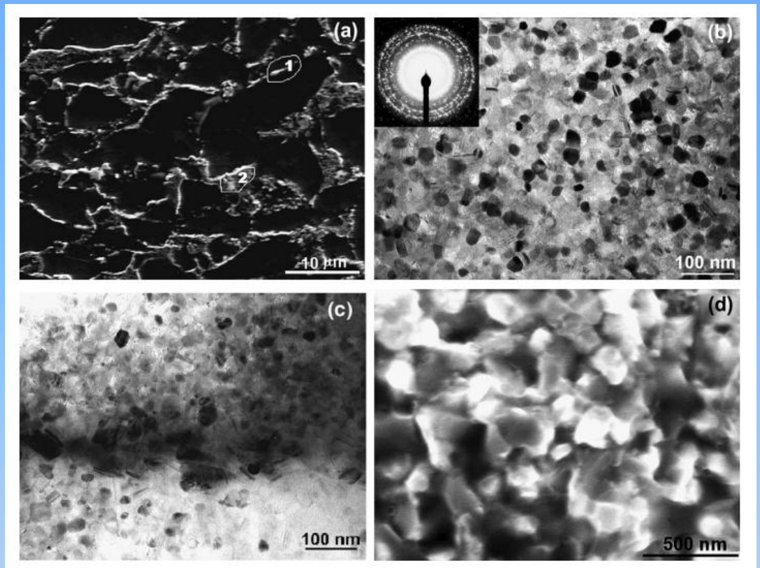
What influences the microstructure of the reaction products?

Powder precursors

Multicomponent amorphous precursors in the reactive SPS in a mixture of nanocrystalline TiO_2 with amorphous Si-C-N to produce $Si_3N_4/SiC/TiC_{0.3}N_{0.7}$



XRD patterns:
a - Si_3N_4-SiC ceramic nanocomposite obtained by SPS of a Si-C-N amorphous precursor
b - Si_3N_4-SiC-$TiC_{0.3}N_{0.7}$ ceramic nanocomposite obtained by **reactive SPS in a mixture of nanocrystalline TiO_2 with amorphous Si-C-N**



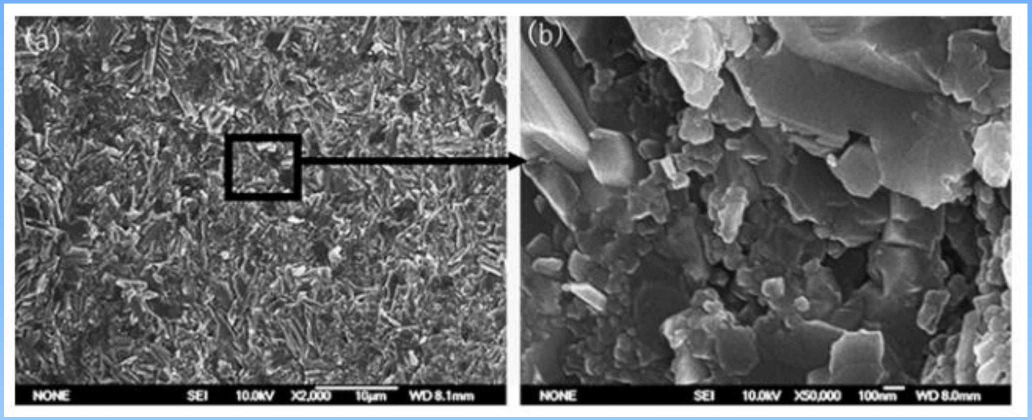
$Si_3N_4/SiC/TiC_{0.3}N_{0.7}$ nanocomposite:
a – fracture surface, SEM
b – microstructure of dark areas in (a) corresponding to the Si_3N_4/SiC, TEM
c – region 1 in (a), TEM
d – region 2 in (a) corresponding to the $TiC_{0.3}N_{0.7}$ phase, SEM

Crystallization of an amorphous phase combined with a reaction: a nanograined reaction product and interesting properties (fracture toughness, metal-like electrical conductivity)

R.G.Duan, J.D.Kuntz, J.E.Garay, A.K.Mukherjee. Scripta Mater. 50 (2004) 1309.

What influences the microstructure of the reaction products?
Powder precursors

Reactive SPS in the Ti-C-Si mixtures of micron-sized powders: conducting a solid state reaction with a complex mechanism



Fracture surface of Ti_3SiC_2–SiC nanocomposite SPS-ed at 1280ºC showing grains of SiC about 100 nm in size
a – lower magnification
b – higher magnification

A phase with grains **as small as 100 nm** can form as a result of solid state reaction between **micron-sized powder reactants**.
Intermediate crystalline phases TiC_x and $Ti_5Si_3C_y$ form from Ti, Si and C and then participate in the reaction $TiC_x + Ti_5Si_3C_y + C \rightarrow Ti_3SiC_2 + SiC$
SiC - **100 nm grains**
Ti_3SiC_2 - 5 μm

The formation of SiC through **intermediate solid phases is crucial for the microstructure development** of the Ti_3SiC_2–SiC nanocomposite from the mixture of coarse-grained powders.

J. Zhang, L. Wang, L. Shi, W. Jiang, L. Chen. Scripta Mater. 56 (2007) 241.

What influences the microstructure of the reaction products?

Powder precursors

Summing up:
the influence of the structure of the initial powder mixtures

We can use the **structure of the powder precursors** as a variable parameter to influence the structure of the resultant product – **similar to conventional reactive sintering** (not in the SPS).

However, **in the SPS** we can **more efficiently** use the potential offered by nanostructured powder precursors in terms of obtaining a fine-grained reaction product.

What influences the microstructure of the reaction products?

Selection of SPS regimes

Reactive SPS: $Ti+6B+C \rightarrow B_4C+TiB_2$

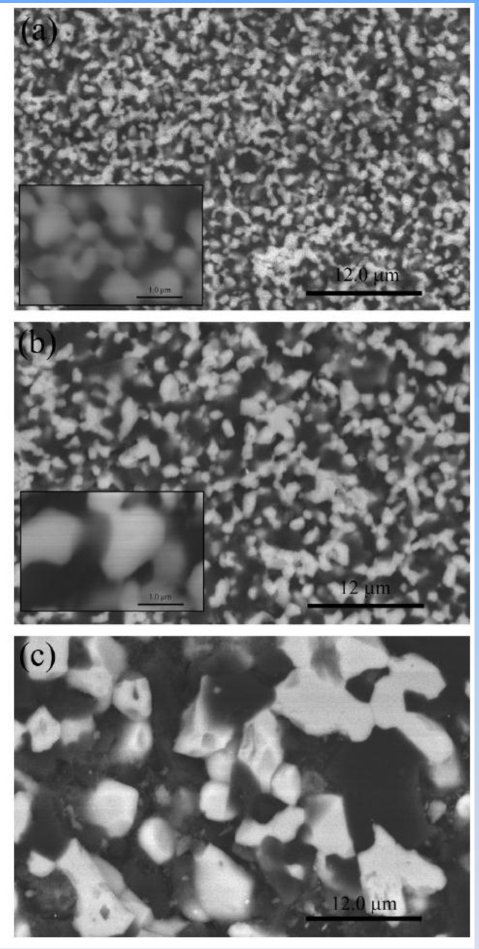
Electric current/temperature

- the microstructure of the in situ B_4C-TiB_2 composites gradually coarsens
- submicron grains can be seen in the sample SPS-ed at 1100 A and having a relative density of 94 %
- the sample of 98% relative density reveals excessive grain growth such that both phases are represented by grains of several microns

a

b

c



B_4C-TiB_2 composites SPS-ed using different electric current values
(a–1100 A, b–1150 A, c–1200 A)

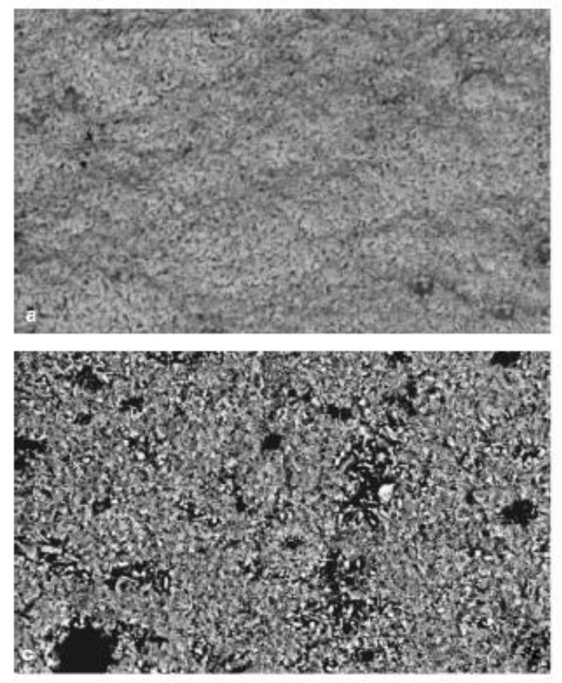
L. Nikzad, R. Licheri, T. Ebadzadeh, R. Orrù, G. Cao. Ceram. Intl. 38 (2012) 6469.

What influences the microstructure of the reaction products?

Selection of SPS regimes

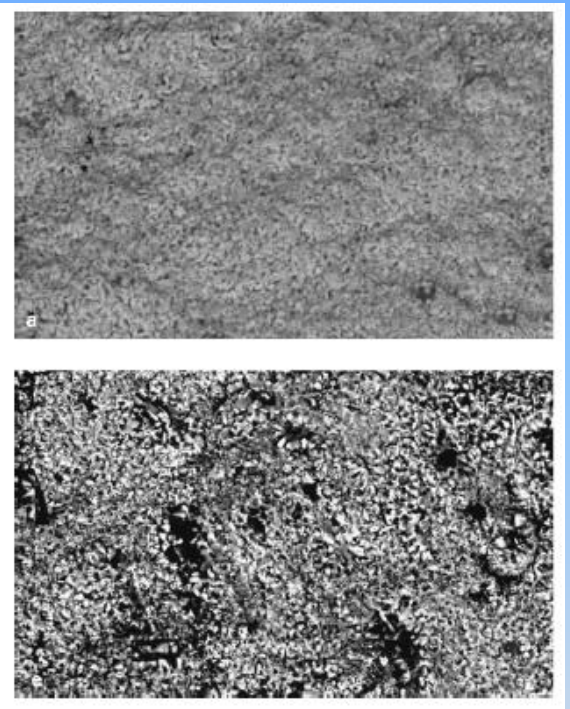
Heating rate

Presence/absence of current



100 K/min

20 K/min



normal SPS run

insulated in BN

Reactive SPS: Ti+2B → TiB_2 in the presence of Mg additions

- a more uniform microstructure at higher heating rates
- a more uniform distribution of the ignition points

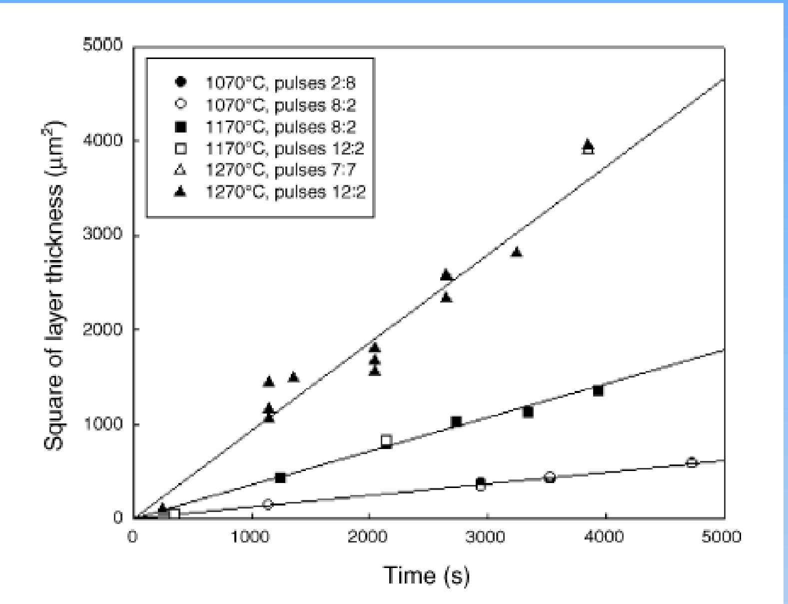
- a more uniform microstructure obtained with the application of electric current

D. Salamon, M. Eriksson, M. Nygren, Z. Shen, J. Amer. Ceram. Soc. 90 (2007) 3303.

What influences the microstructure of the reaction products?

Selection of SPS regimes

Pulsing pattern



Mo-Si foils:
no effect on reactivity in the reaction
$Mo+Si \rightarrow MoSi_2$

W. Chen, U. Anselmi-Tamburini, J.E. Garay, J.R. Groza, Z.A. Munir. Mater. Sci. Eng. A 394 (2005)132.

But there may be an effect on densification of the reaction product as in sintering without reaction.

Pressure

To enhance densification of the reaction products.

Challenges of producing dense fine-grained materials

The microstructure development during the reactive SPS follows one of the two possible scenarios:

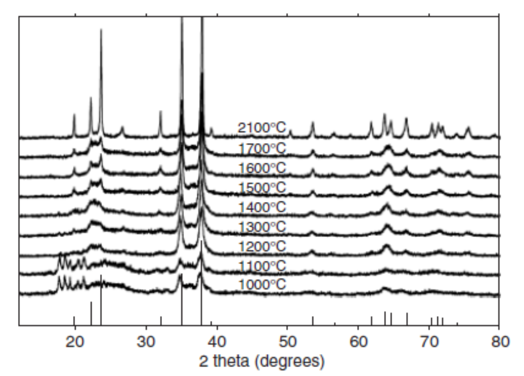
1) simultaneous reaction and densification
2) complete reaction followed by densification (if the latter is aimed at) at higher temperatures.

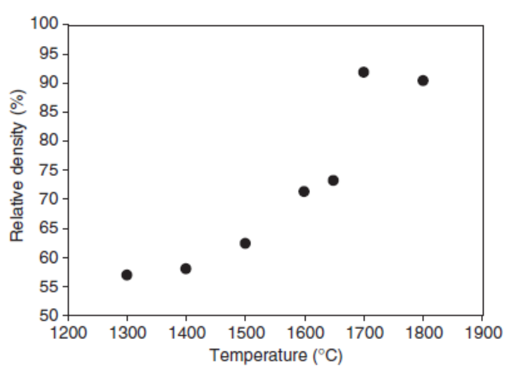
A chemical reaction within a narrow temperature range during SPS accompanied by shrinkage of the sample is the best situation for the formation of a dense nanostructured product.

Z. A. Munir. J. Mater. Synth. Proc. 8 (2000) 189.

If the reaction and densification steps **do not coincide**, in order to obtain a fully-dense product, one has to resort to higher-temperature sintering.

Synthesis of B_4C from B and C: reaction is complete at 1200 C densification at 1900 C





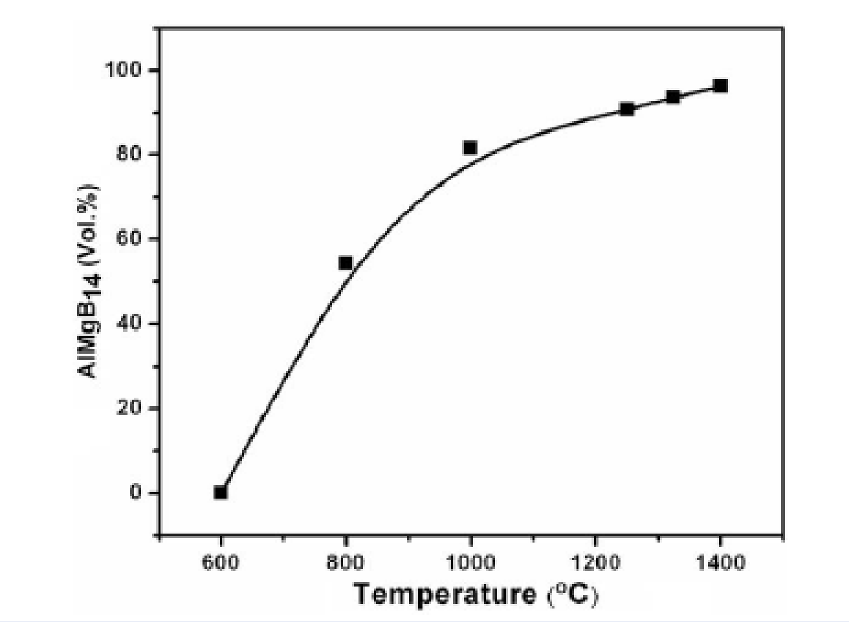
U. Anselmi-Tamburini, Z. Munir, Y. Kodera, T. Imai, M. Ohyanagi. J. Amer. Ceram. Soc. 88 (2005) 1382.

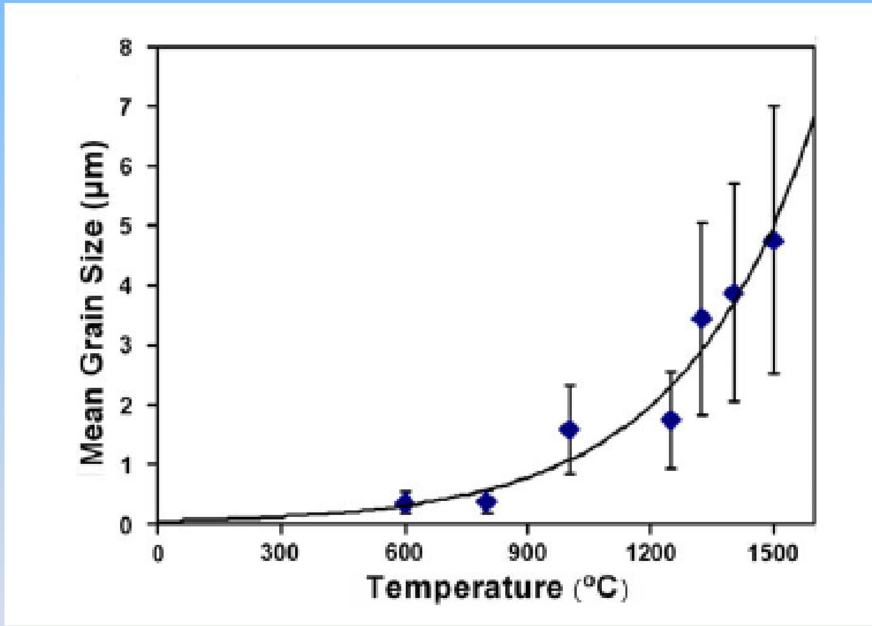
Challenges of producing dense fine-grained materials

Slow reactions occurring gradually during heating

The upper temperatures of the range destroy the nanostructure of the synthesized product formed at the initial heating stages.

Synthesis of $AlMgB_{14}$ in the SPS in a mechanically milled mixture of Al, Mg and B





D.J. Roberts, J. Zhao, Z.A. Munir. Intl. J. Refractory Metals Hard Mater. 27 (2009) 556.

Challenges of producing dense fine-grained materials

Summing up:
why do these problems exist?

- The reaction is complete at lower temperatures than required for efficient densification of the product (diffusion in the product is too slow).

- During the reactions that occur gradually upon heating of the powder mixtures in the SPS, the initially formed grains of the products tend to grow at the upper temperatures of the range.

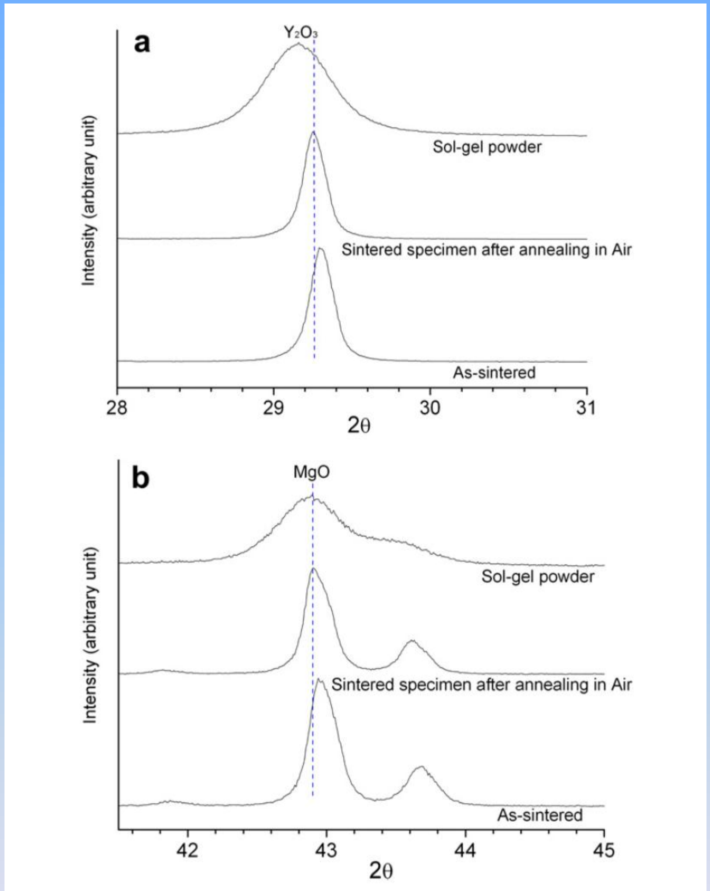
- The reaction product has already established contacts between the particles (agglomerated product), which are too strong to allow for the particle rearrangement.
The importance of the interparticle contacts
E. Olevsky, I. Bogachev, A. Maximenko. Scripta Mater., 2013.

- In multiphase products, the phases may have different sintering behavior (plays a significant role if the phases are not mixed at the grain scale and form agglomerates).

Undesirable chemical reactions in the SPS

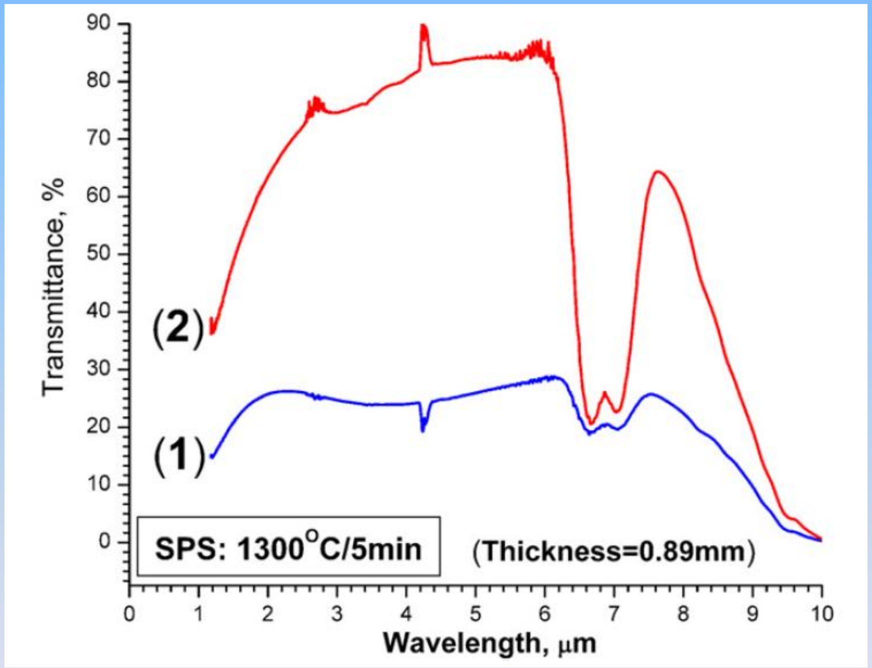
Chemical reduction of oxides

SPS of MgO-Y_2O_3 composites: oxygen losses in both oxides



XRD patterns of the Y_2O_3-MgO nanocomposites: powders, SPS-ed and annealed in air after the SPS showing the shift of the peak positions of both oxides

Low infra-red transmission of the SPS-ed Y_2O_3-MgO nanocomposite was improved when the oxygen content was restored by annealing in air after the SPS



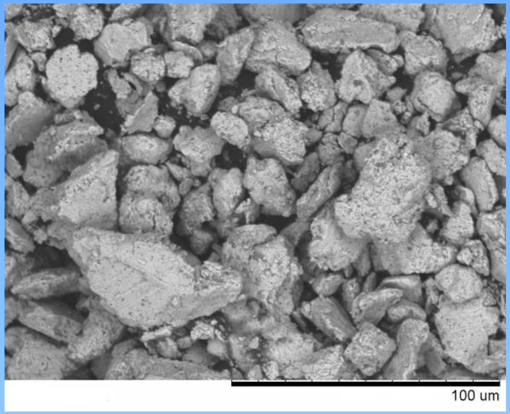
Transmission spectra of SPS-ed Y_2O_3-MgO nanocomposite (1) and after annealing in air (2)

D. Jiang and A. K. Mukherjee, Scripta Mater. 64 (2011) 1095.

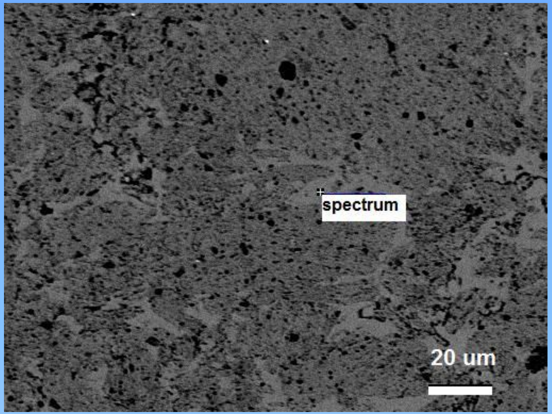
Undesirable chemical reactions in the SPS

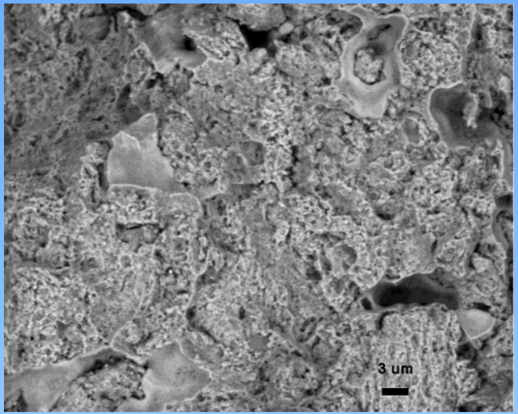
Interfacial reactions in composites

SPS of 18 vol.% Ti_3SiC_2-Cu composites



18 vol.% Ti_3SiC_2-Cu composite powder





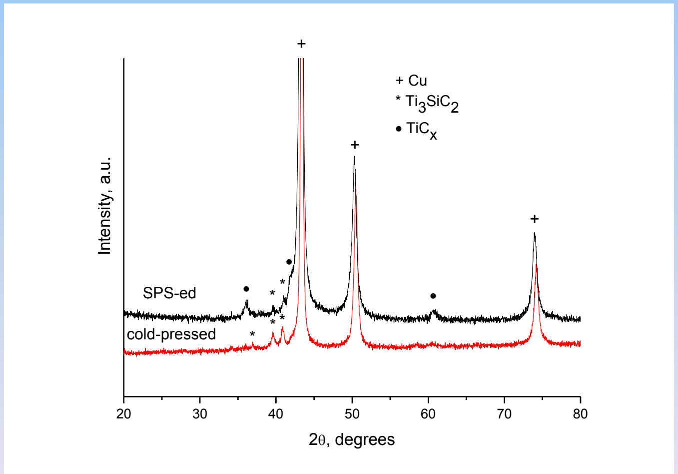
SPS-ed 18 vol.% Ti_3SiC_2-Cu composite
(a – polished cross-section and b - fracture surface)

- high hardness of 18 vol.% Ti_3SiC_2-Cu prevents the formation of an intimate contact between the composite particles during the early sintering stages under the chosen pressure (40 MPa)

The interfacial reaction

$Ti_3SiC_2 + Cu \rightarrow TiC_x + Cu(Si)$

- occurs in the vicinity of contacts between the powder particles (areas, in which the Cu matrix melts)
- melting of Cu is caused by the formation of local high-temperature regions



XRD patterns of the cold-pressed and SPS-ed 18 vol.% Ti_3SiC_2-Cu compacts

D.V. Dudina, V. I. Mali, A. G. Anisimov, N. V. Bulina, M. A. Korchagin, O. I. Lomovsky, I. A. Bataev, V. A. Bataev. Metals Mater. Intl., accepted.

D. V. Dudina, A. K. Mukherjee. Reactive Spark Plasma Sintering: successes and challenges of nanomaterial synthesis, J. Nanomater., submitted.

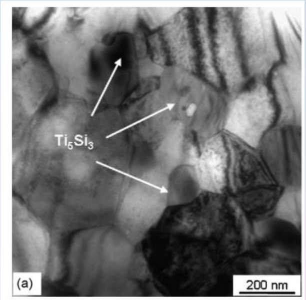
Materials with valuable properties obtained by reactive SPS: examples

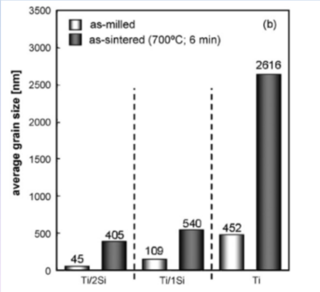
Fracture-tough fine-grained ceramics

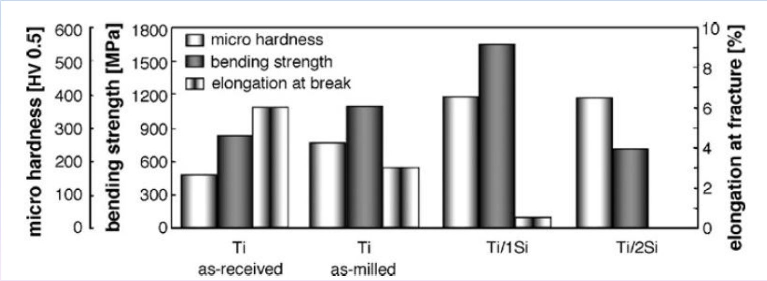
Materials	Properties	References
TiB_2 with needle-shaped grains	High fracture toughness 5.9 MPa·m$^{1/2}$	Z. Zhang Z, X. Shen, F. Wang, S. Lee, J. Amer. Ceram. Soc. 94 (2011) 2754.
TiN-TiB_2	High fracture toughness 6.5 MPa·m$^{1/2}$	J. W. Lee, Z. A. Munir, M. Shbuya, M. Ohyanagi, J. Amer. Ceram. Soc. 84 (2001) 1209.
Si_3N_4-SiC-$TiC_{0.3}N_{0.7}$	High fracture toughness 6.7 MPa·m$^{1/2}$ Metal-like conductivity	R.G.Duan, J.D.Kuntz, J.E.Garay, A.K.Mukherjee. Scripta Mater. 50 (2004) 1309.
$MoSi_2$	High fracture toughness 5.8 MPa·m$^{1/2}$ Improved oxidation resistance	G. Cabouro, S. Chevalier, E. Gaffet, Y. Grin, F. Bernard. J. Alloys Comp. 465 (2008) 344.

Metal matrix composites of improved strength and thermally stable microstructures

Ti-Ti_5Si_3 composites : reduced grain size, improved strength







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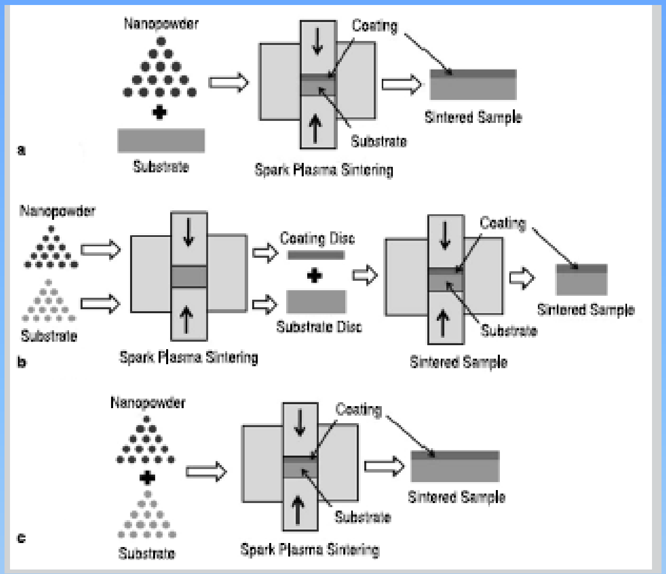
Future uses of reactive SPS for the synthesis and design of novel materials

- Preparation of nanostructured materials using chemical reactions of decomposition
- Synthesis in the dies of new geometry and in modified die/punch set-ups to produce different shapes and microstructures
- Low-pressure SPS for making porous bodies of controlled porosity from the reaction products
- Gradient materials
- Coatings containing phases formed in situ
- Joining of materials

D. V. Dudina, A. K. Mukherjee. In: Nanotechnology, vol.4: Nanomaterials and Nanostructures, Studium Press LLC, USA, 2013, pp. 237-264.



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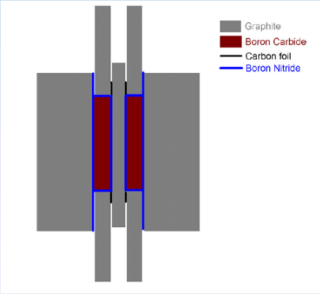

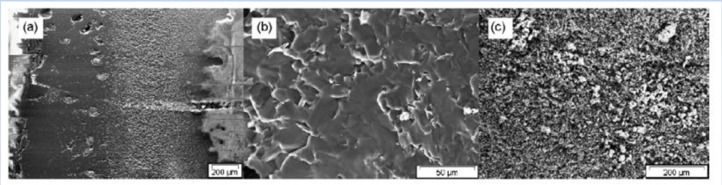

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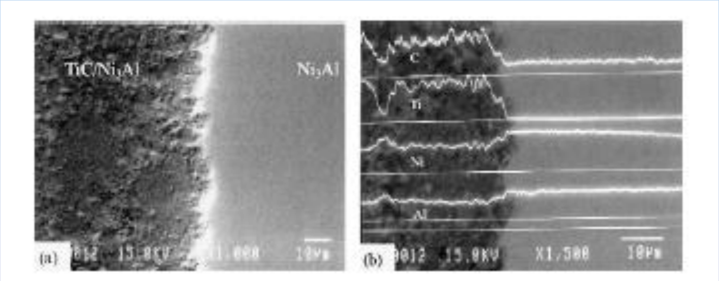

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Summary

Initially developed for conducting solid state sintering, Spark Plasma Sintering has been proved to be an attractive method of solid state synthesis.

The fine-grained microstructure of the reaction products is favored when

- the reactants are mixed at the nanolevel
- multi-step reactions are carried out.

The best scenario for obtaining **a dense fine-grained material** by reactive SPS is simultaneous reaction and densification: the reaction in the system should start at temperatures high enough to sinter the reaction product to high relative densities.
When the reaction is complete at temperatures too low for densification, higher temperatures are required to produce a dense material, which sacrifices the as-synthesized nanostructure.

Undesirable chemical reactions (interfacial reactions between phases in composites) are possible during the SPS, but can be prevented or allowed to occur to a controlled extent.

SPS is currently becoming a new synthesis method in solid state chemistry and a materials design tool at nano-, micro- and macro-scales.

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Thank you!

Our recent publications on reactive SPS

Book Chapters

D. V. Dudina, A. K. Mukherjee. Reactive Spark Plasma Sintering for the production of nanostructured materials. **Nanotechnology, vol.4: Nanomaterials and Nanostructures,** Eds. S.Sinha & N.K.Navani, Studium Press LLC, Houston, USA, 2013, pp. 237-264.

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2. D.V. Dudina, V. I. Mali, A. G. Anisimov, N. V. Bulina, M. A. Korchagin, O. I. Lomovsky, I. A. Bataev, V. A. Bataev. Ti_3SiC_2-Cu composites by mechanical milling and Spark Plasma Sintering: possible microstructure formation scenarios. **Metals Mater. Intl.**, accepted for publication.
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