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Plasma chemical synthesis of multicomponent nanopowders, their characteristics, and processing

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Outline

- Introduction – nanoparticles, their preparation methods
- Experimental
  - synthesis of multicomponent nanoparticles by using RF plasma
  - characteristic features of produced particulate composites
  - processing by hot pressing and SPS sintering.
- Conclusions

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Application of nanoparticles

Nanotechnology

Nanoparticles , nanowires , thin films , carbon nanotubes

- Nanostructured materials
  - Engine parts
  - Cutting tools
  - High -temperature ceramics
  - Advanced coatings
  - Polymer matrix composites
  - Metal -matrix composites
- Electronics
  - Optoelectronic devices
  - Phosphorus
  - Multilayer capacitors
  - Manomagnetic fluids
  - Data storage
  - Energy storage
  - Sensors
  - Fuel cells
- Nano -biotechnology
  - Biomaterials , implants
  - Antimicrobial wound dressing
  - Drug delivery
  - Human health monitoring
- Nano -systems
  - Catalysts
  - Chemical sensors
  - Pigments
  - UV radiation protection
  - Abrasion , corrosion protection
  - Reinforcement , fillers
  - Flame retardants
  - Self -learning glasses , textiles
  - Propellants

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Preparation methods of nanoparticles

■ Mechanical solid state phase processing	Mechanical milling Mechanical alloying Mechanical-chemical processing Plastic deformation
■ Liquid phase processing	Sol-gel processing Chemical hydroxide precipitation Hydrothermal synthesis Combustion synthesis
■ Gas phase processing	Inert gas condensation Laser synthesis DC, RF, microwave plasma synthesis

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Application of multicomponent nanoparticles

- Improvement of mechanical, physical and chemical characteristics
- Preparation of uniform mixtures of refractory compounds with sintering additives
- Catalysts
- Doped nanoparticles for microelectronics and luminiscent materials

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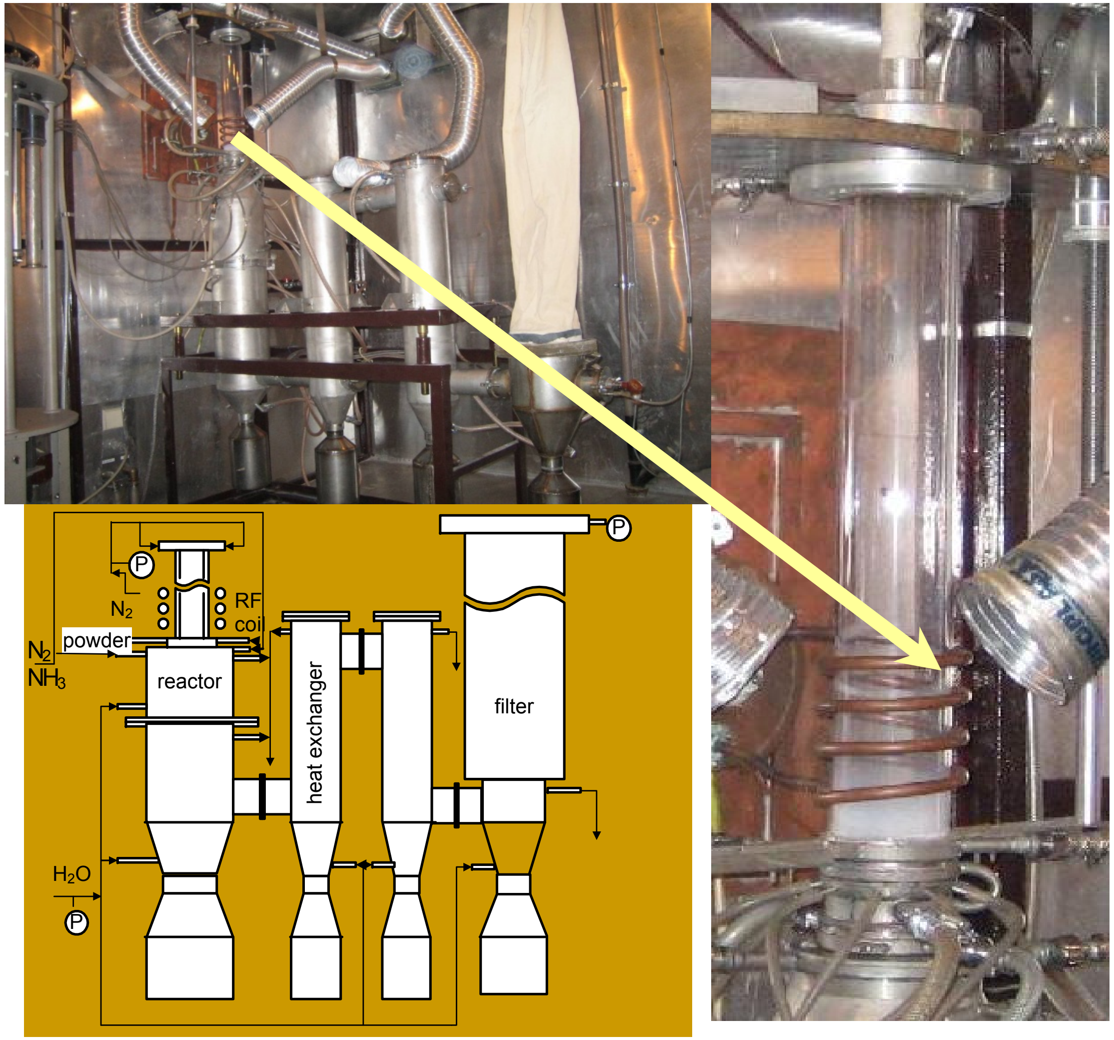
Plasmachemical synthesis

based on formation of product from a vapour phase

provides an attractive alternative for producing multicomponent compounds or particulate composites

due to mixing of component at molecular level and relative high production rate of a simple one-stage process.

Plasma apparatus for producing nanoparticles Institute of Inorganic Chemistry RTU



RF plate power	70-100 kW
Frequency	5.28 or 1.2 MHz
Plasma forming gas flowrate	8.0-9.0 m^3/h
Quenching gas flowrate	1.5-8.0 m^3/h
Feeding rate of powders	0.6-1.8 kg/h

Necessary conditions for preparation of nanosized powders of refractory compounds

1. Complete evaporation of raw materials determined by:
   - plasma parameters and temperature distribution
   - particle size of raw materials and their injection mode
2. Controlled growth rate and time of product particles determined by:
   - concentration of particles in plasma flow
   - melting and boiling temperature of product particles
   - cooling rate of products
   - velocity of plasma flow
   - ratio and quantity of products components
3. Elimination growth of precursor particles or extra phases started at higher temperature and promotion formation of product particles by changing temperature and reaction agents

Characteristics of prepared nitride-based particulate composites

Reactants	Products		
	SSA, m^2/g	Phase compositions	Morphology of particle
	Nitride-Metal		
Ti, Ni, Co, Fe, N_2 Ti, Cr, W, N_2	16-40 14-40	TiN, Ni, Co, Fe TiN, Cr, Cr_2N, W	TiN cubic crystals coated with metal droplets
Ti, Mo, N_2	18-35	TiN, Mo, Mo_2N	TiN rod-like particles
Al, Mo, N_2 Al, Cr, Fe, N_2	24-36 20-35	AlN, Mo AlN, Cr_2N, Cr, Fe	AlN whiskers with Mo, Cr, Fe, Cr_2N droplets
	Nitride-Nitride		
Ti, Al, N_2, NH_3 Zr, Al, N_2, NH_3	18-40 16-36	TiN, AlN ZrN, AlN	TiN or ZrN cubic crystals coated with AlN
Al, Si, NH_3, N_2 Ti, Si, NH_3, N_2 Zr, Si, NH_3, N_2	26-70 24-60 20-50	AlN, Si_3N_4 TiN, Si_3N_4 ZrN, Si_3N_4	AlN, TiN or ZrN crystals coated with Si_3N_4

Reactants	Products		
	SSA, m^2/g	Phase compositions	Morphology of particle
	Nitride-Carbide		
Si, CH_4, NH_3, N_2	24-60	Si_3N_4, SiC	SiC particles coated with Si_3N_4
Ti, CH_4, N_2	18-40	$TiN_{0.6}C_{0.4}$	Cubic particles
WO_3, CH_4, N_2	22-30	W_2C, WC_{1-x}	
	Nitride-Fluoride		
Al, CaF_2, NH_3, N_2 Al, YF_3, NH_3, N_2	20-35 20-35	AlN, CaF_2 AlN, YF_3	AlN hexagonal plates, CaF_3, YF_3 spherical particles
	Nitride-Oxide		
Al, CaO, NH_3, N_2 Al, Y_2O_3, NH_3, N_2	24-35 24-35	AlN, CaO AlN, Y_2O_3, YN	AlN hexagonal plates, CaO, Y_2O_3 spherical particles
Si, Y_2O_3, Al_2O_3, NH_3, N_2 Si, SiO_2, Al, Al_2O_3, N_2, NH_3	30-70 30-90	Si_3N_4, Y_2O_3, Al_2O_3, YSi_2 β-$Si_{6-x}Al_xO_xN_{8-x}$	Unregular-shaped particles

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Characteristics of nanosized oxides and their composites

Raw powders	As prepared		After annealing		
	SSA, m^2/g	Phase composition	T, °C	SSA, m^2/g	Phase composition
ZrO_2, Y_2O_3	18-36	t-ZrO_2, m-ZrO_2, c-ZrO_2	1300	2-10	t-ZrO_2, m-ZrO_2, c-ZrO_2
Al_2O, ZrO_2, Y_2O_3	20-50	δ-Al_2O_3, t-ZrO_2, m-ZrO_2	1150	12-18	α-Al_2O_3, t-ZrO_2, m-ZrO_2
$3Al_2O_3.2SiO_2$-ZrO_2	33	m-, t-ZrO_2	1300	16	$3Al_2O_3.2SiO_2$, m-, t-ZrO_2
NiO, ZrO_2, Y_2O_3	16-30	NiO, t-, c-ZrO_2	1200	2-4	NiO, c-ZrO_2
Al_2O_3, NiO	35-56	$NiAl_2O_4$, NiO	1200	18-32	$NiAl_2O_4$, NiO
Al_2O_3, MgO	35-60	$MgAl_2O_4$	1200	8-16	$MgAl_2O_4$
Al_2O_3, SiO	35-48	X-ray amorph	1300	15-20	$3Al_2O_3$*$2SiO_2$, δ-Al_2O_3
Al_2O_3, CoO	30-48	$CoAl_2O_4$, $Co_2Al_2O_4$	1200	6-28	$CoAl_2O_4$, $Co_2Al_2O_4$
Al-Na-Li-O	16-36	β-,β''-Al_2O_3, $Al(OH)_3$, m-Al_2O_3	1200	14-20	β''- Al_2O_3, β- Al_2O_3 (tr.)
Fe_2O_3, NiO	20-36	$NiFe_2O_4$	…	…	…
Zn-O, Eu_2O_3	16-28	ZnO			
CoO, FeO	32	$CoFe_2O_4$	…	….	…

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Main features of multicomponent powders

- Formation of coated particles
- Change of chemical characteristics
- Change of particle shape
- Change of phase composition
- Dependence of specific surface area and particle size on the ratio of components

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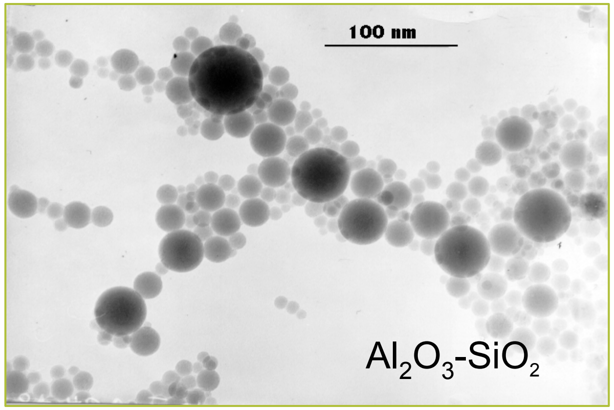
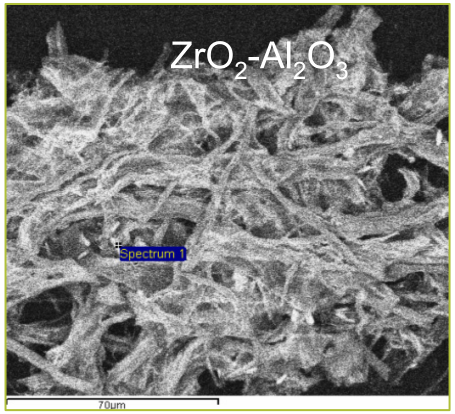
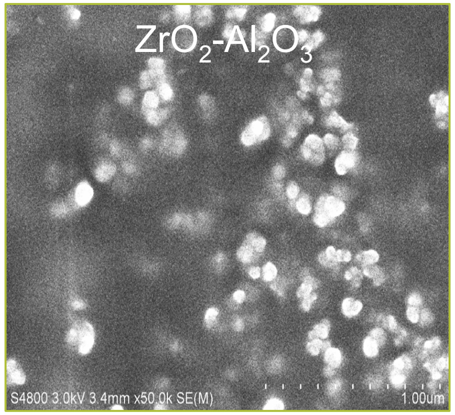
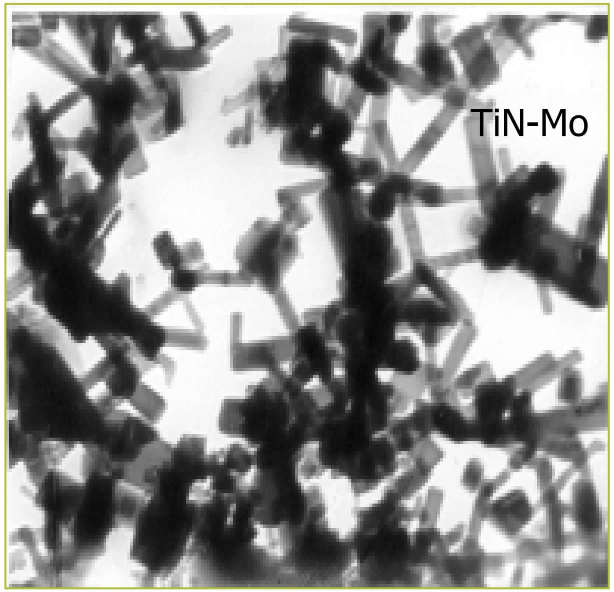
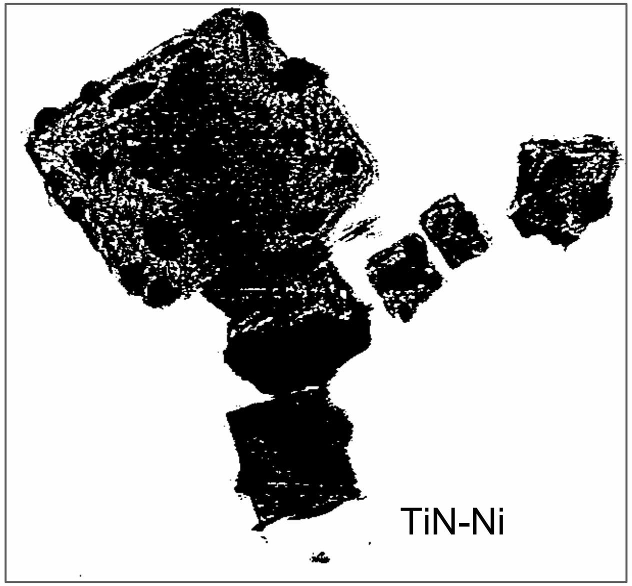
Micrographs of particles

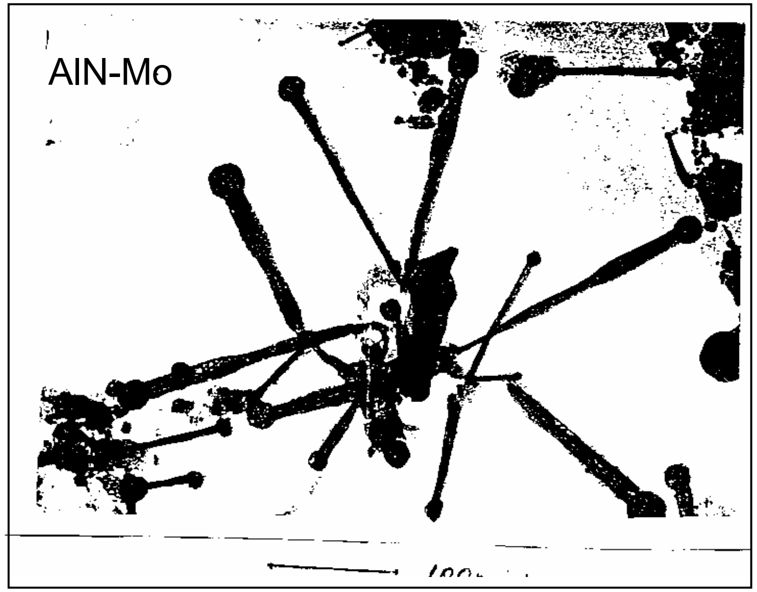












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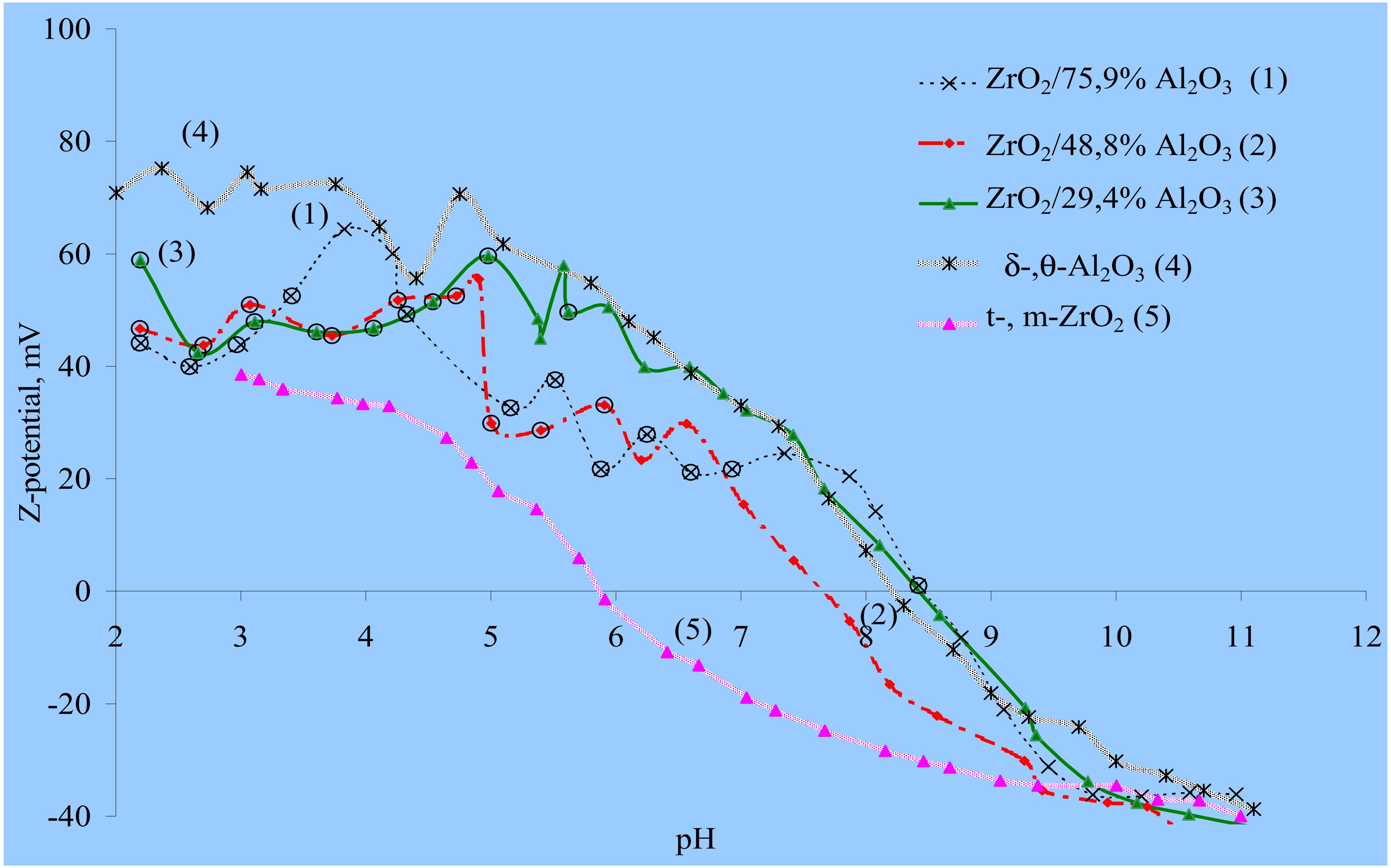
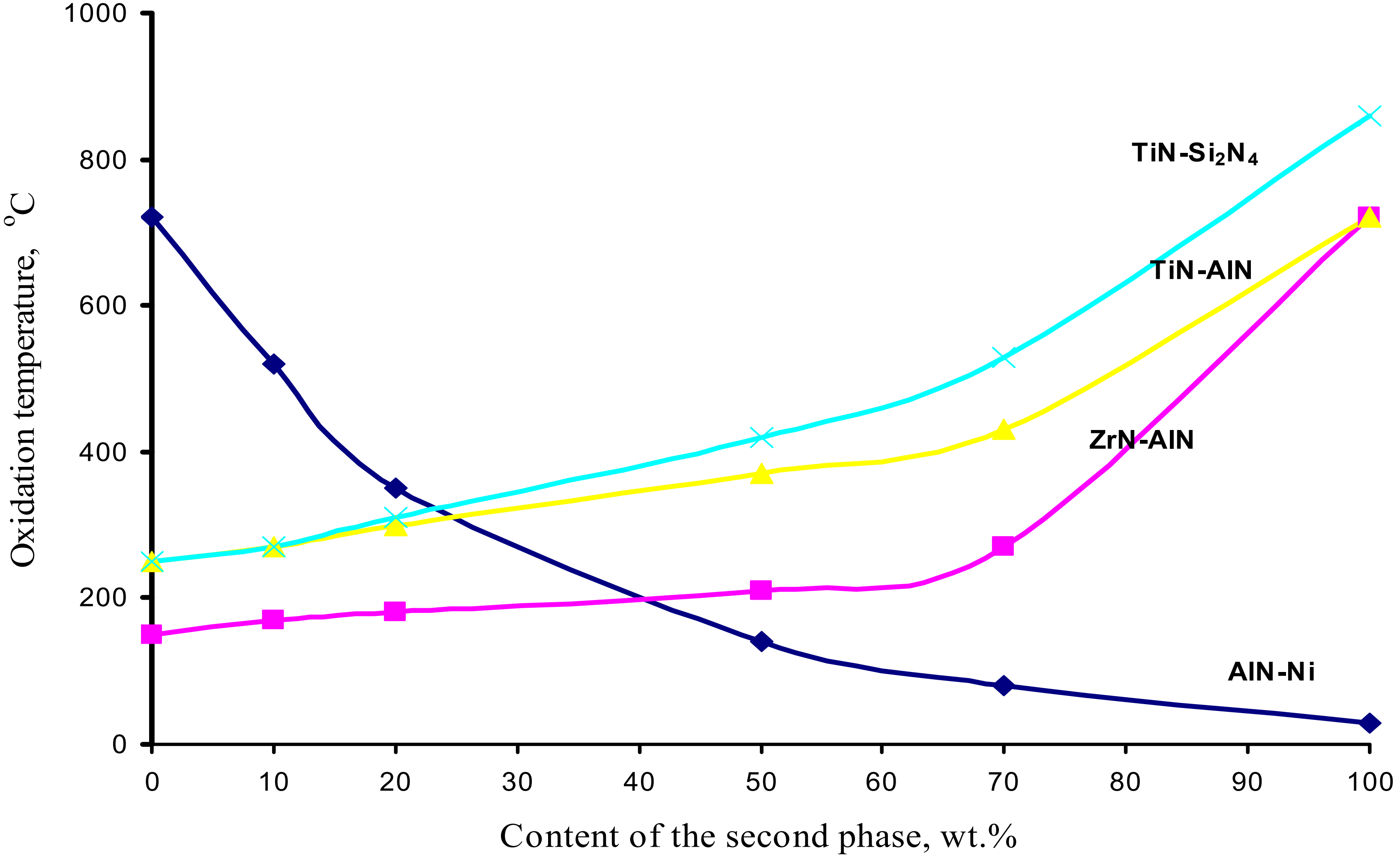
Z-potential curves of ZrO_2, ZrO_2-Al_2O_3, and Al_2O_3



Dependence of oxidation temperature of particulate composites on content of the second phase



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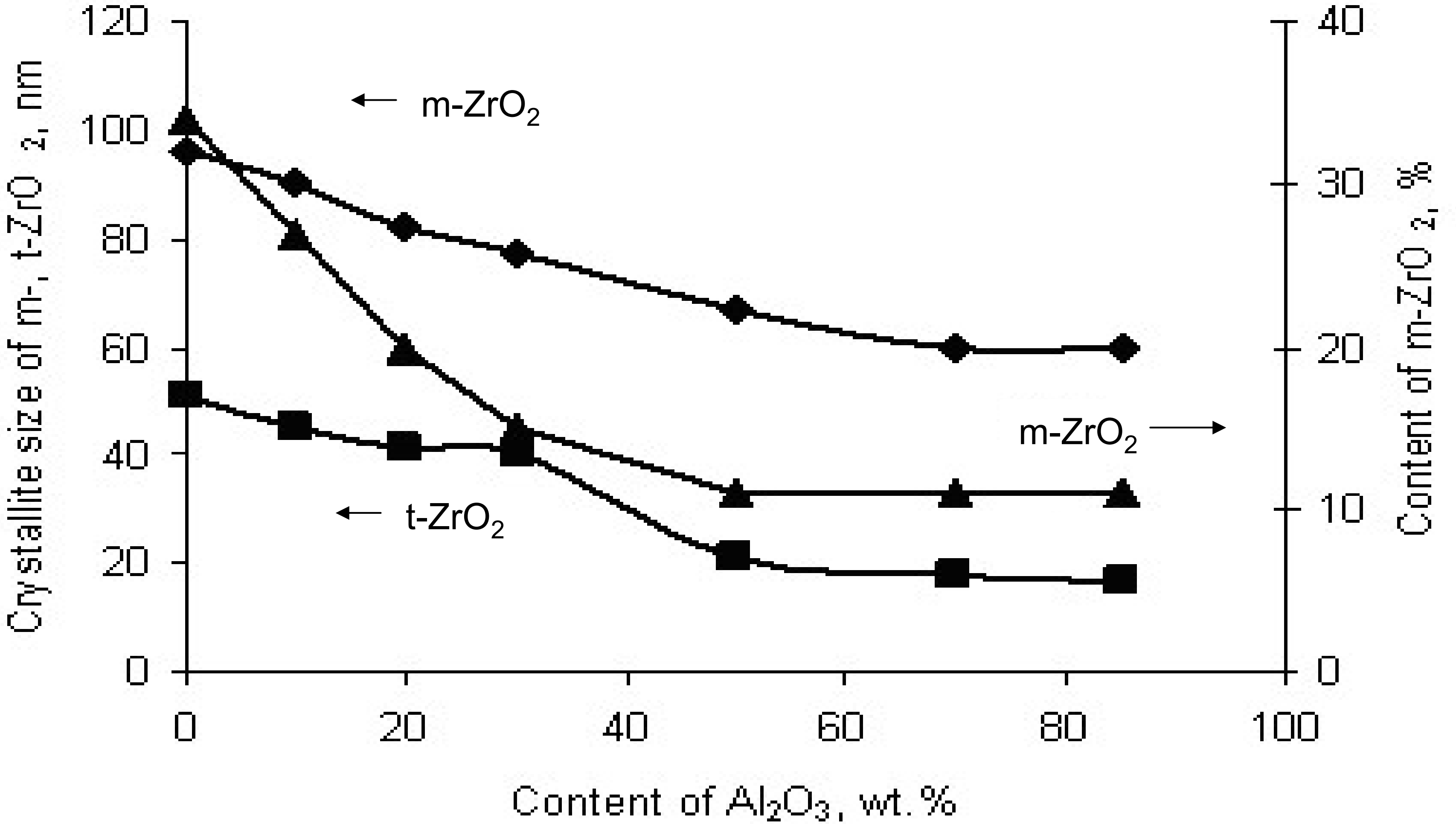
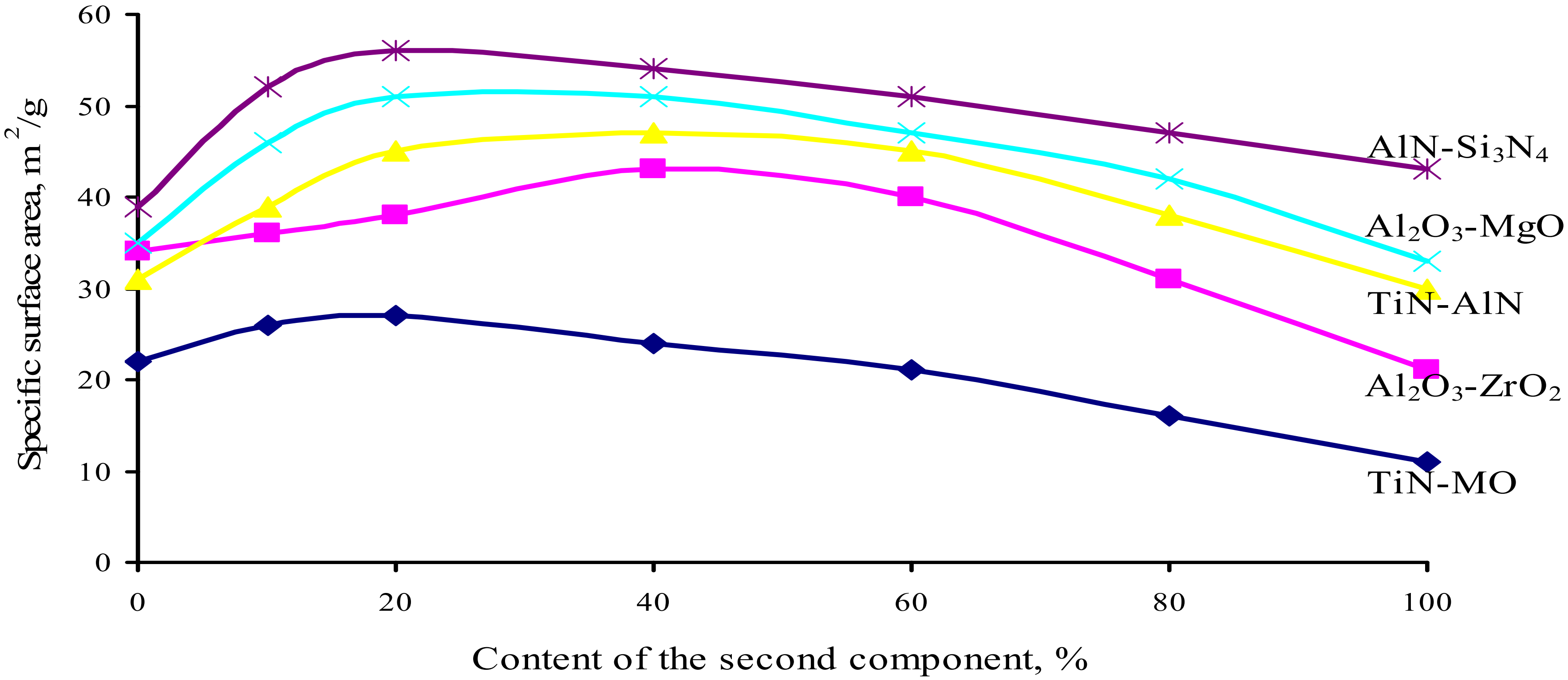
Dependence of crystallite size and content of m-ZrO_2 phase on the contentration of Al_2O_3



Dependence of SSA of particulate nanocomposites powders on the content of second phase



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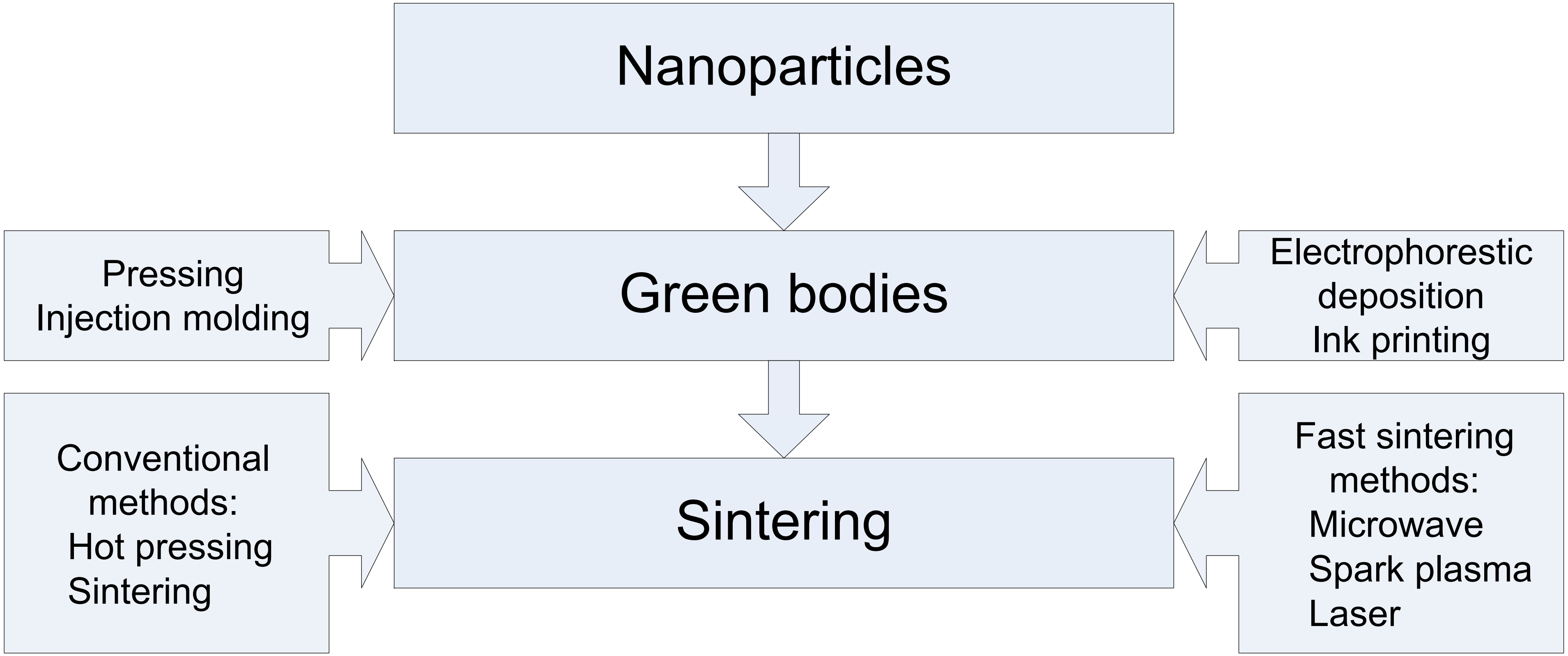
Densification methods of nanoparticles



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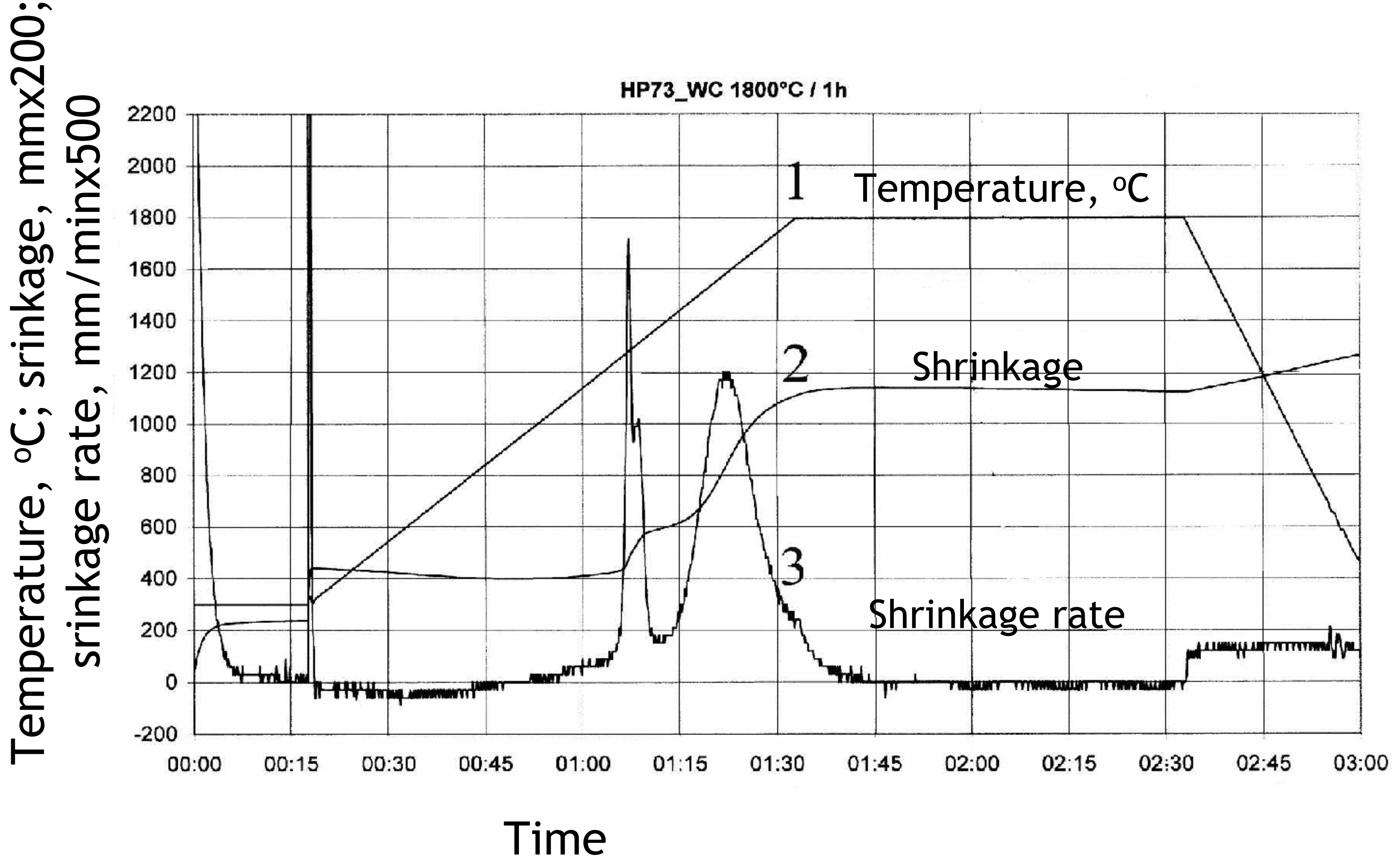
Sintering methods

Nanoparticles are consolidated

- by using hot pressing at 1500–1900 °C
- by using spark plasma sintering (SPS, Sojitz Corp.) technique at 1400–1900 °C; applied pressure of 30 MPa is selected and maintained constant

WC hot pressing process parameters



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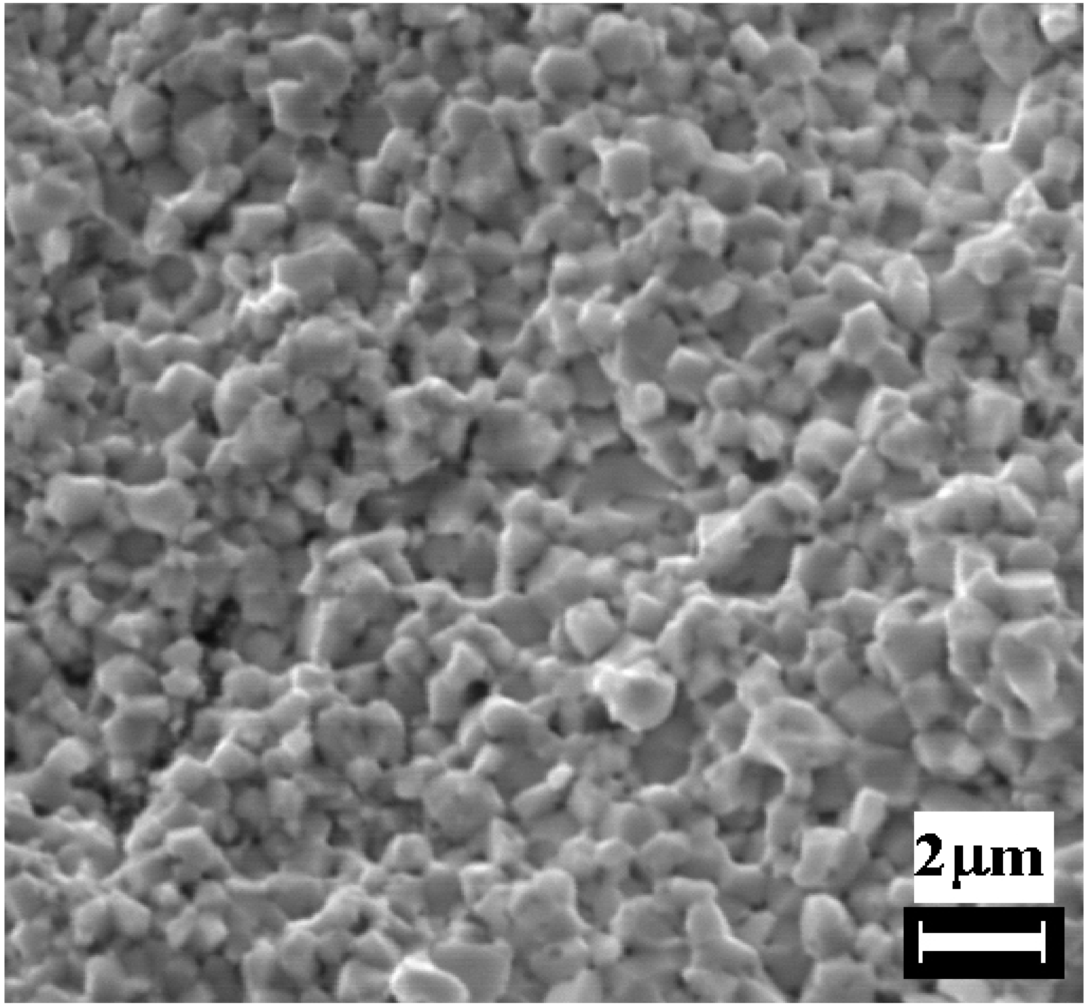
Microstructure of hot-pressed WC



HP73_WC 1800 ^{o}C/1 h

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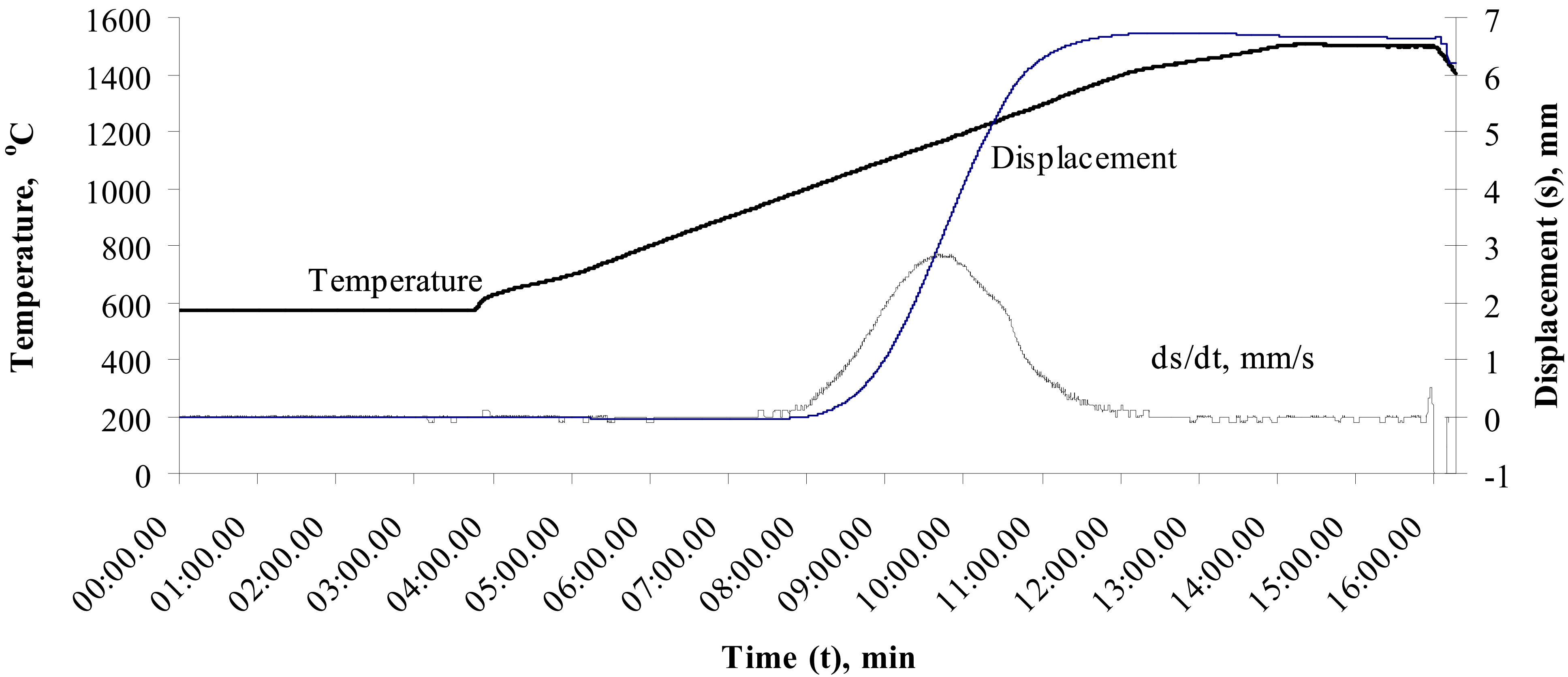
Parameters of SPS process of YAG nanopowders



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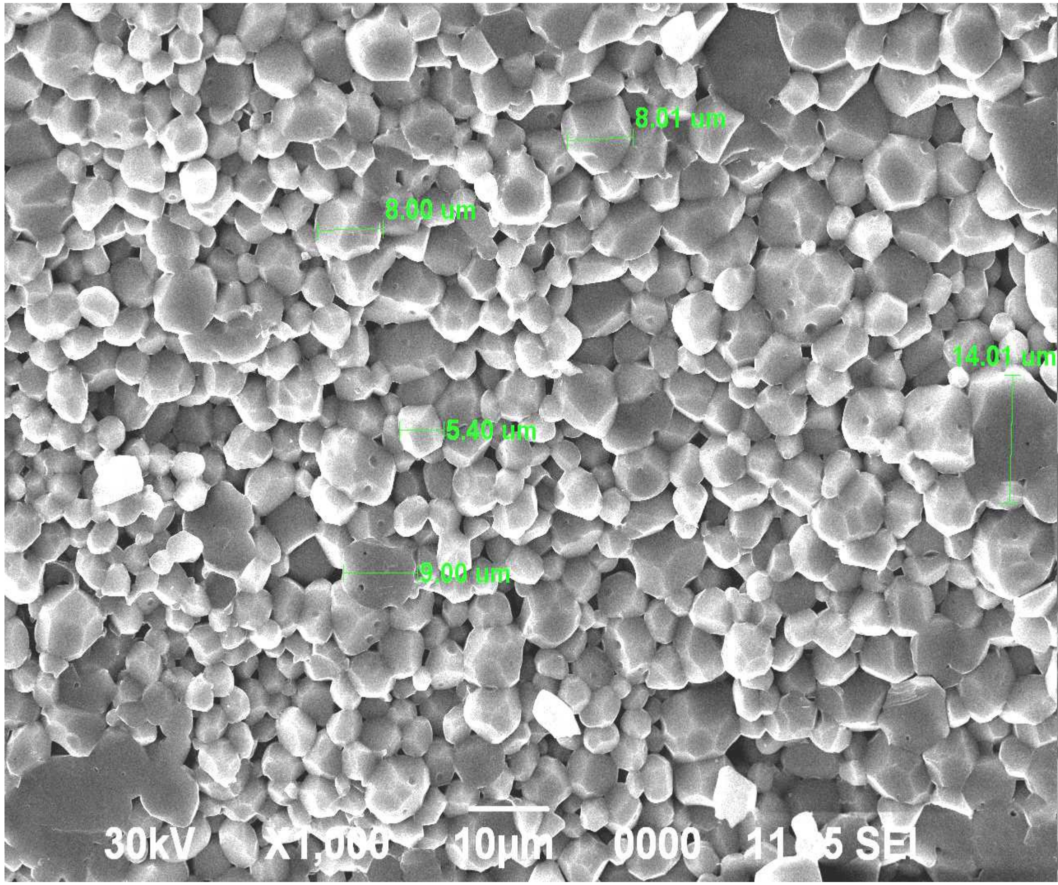
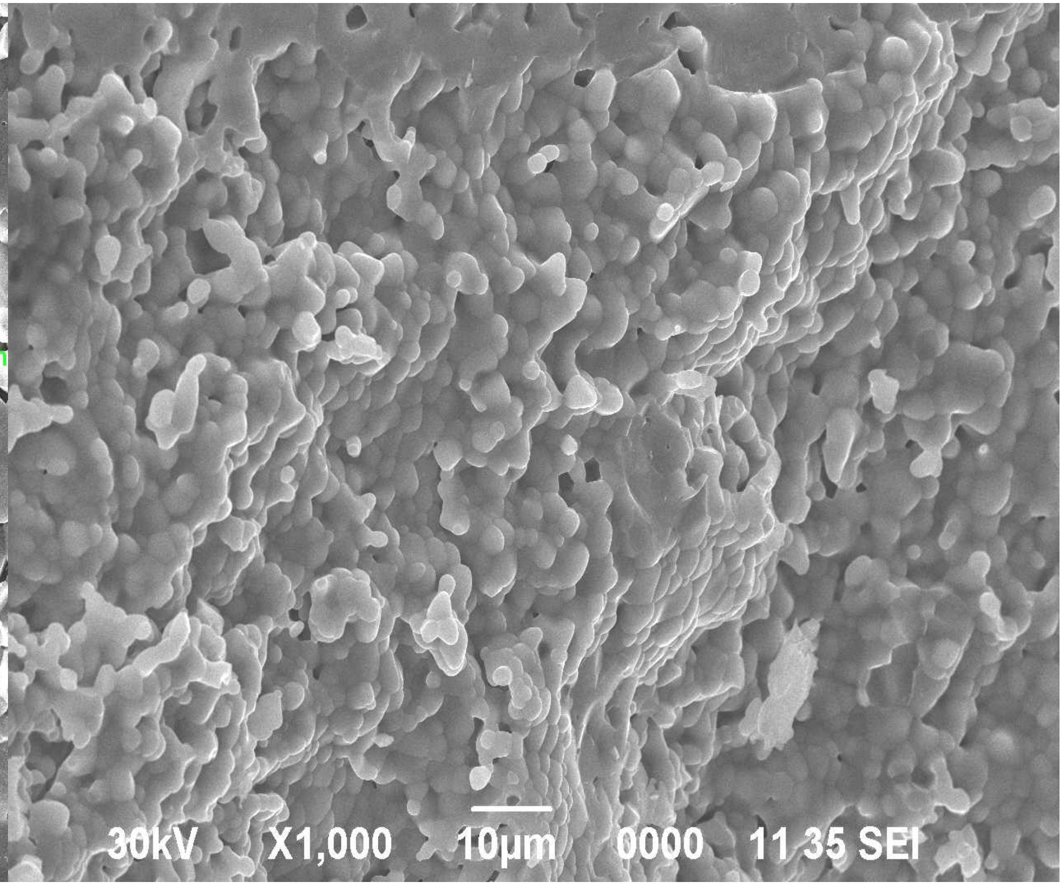
SEM images of fracture surface of $Y_3Al_5O_{12}$ samples



Spark plasma sintering



Conventional pressureless sintering

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Conclusions

1. Plasmachemical synthesis have been applied successfully for producing nitride-metals, nitride-carbide, nitride-oxide, oxide-oxide, oxide-metals particulate nanocomposites by introducing and evaporation of coarse-grained commercially available powders of chemical elements, oxides, and salts in nitrogen or air plasma.
2. Synthesis of multicomponent particulate composites in thermal plasma influences particle shape, phase composition, specific surface area with respect to single particle.
3. Spark plasma sintering of the multicomponent particulate nanocomposites intensifies densification with respect to hot pressing or pressureless sintering but also accelerates grain growth.

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