GSM

Processing of Nanostructured Ceramics:

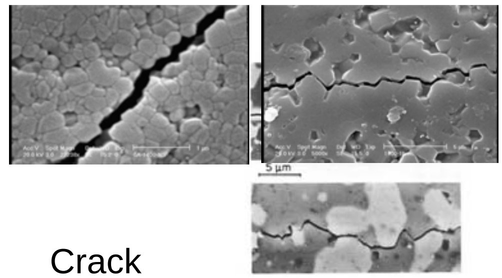
Shaping, Sintering and Properties

Mehdi Mazaheri

Nov 2009

Introduction (1)- Ceramics?

Toughening Mechanism in Ceramics



Crack deflection

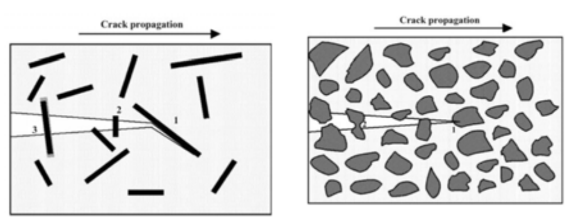
Peng et al., J. Am.Cerm.Soc., 1988

Introduction - Ceramics?

low density, low sensitivity to corrosion, high rigidity and hardness even at high temperature

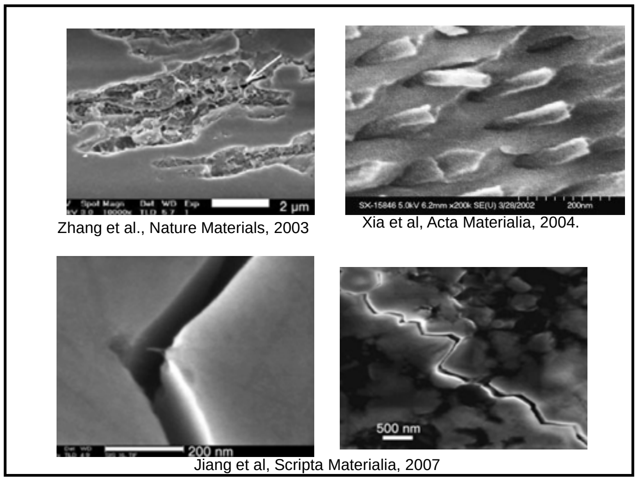
Introduction (1)- Ceramics?

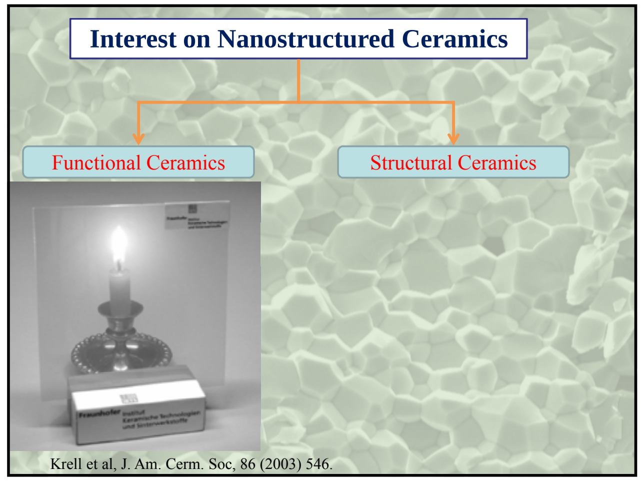
Toughening Mechanism in Ceramics



(1) Crack deflection
(2) Crack bridging
(3) Fibers pullout

(1) Crack blunting
(2) Crack bridging





Introduction (1)- Ceramics?

Grain refining

Increasing of fracture toughness at room temperature

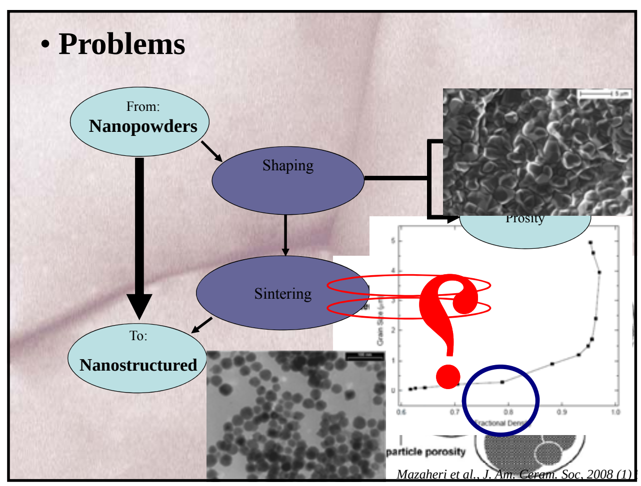
High temperature mechanical properties
(G.B. sliding accommodated by diffusion or interface reaction mechanisms)

$$\dot{\varepsilon}(\sigma,T) = A\left(\frac{\sigma-\sigma_0}{G}\right)^n \left(\frac{b}{d}\right)^p D$$

Nano-structured ceramics reinforced by nano-particles or fibers

Higher creep resistance
(Ionascu, EPFL Thesis, 2008)

3 times higher fracture toughness
(Zhang et al, Nature Materials, 2003)



Shaping?

ششمین کنگرهٔ سرامیک ایران — ۲۵ و ۲۶ اردیبهشت ۱۳۸۶

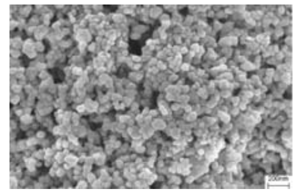
مطالعه چگالش نانوذرات آلومینا در اثر بارگذاری تک محوری و تف جوشی

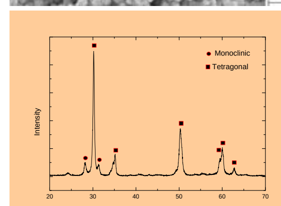
زهره رضوی حسابی، مهدی مظاهری و سید خطیب الاسلام صدرنژاد

mmazaheri@gmail.com

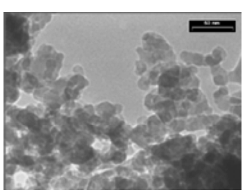
Sintering of n-3Y.TZP

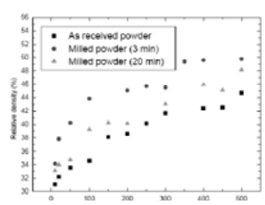
Master Sintering Curve

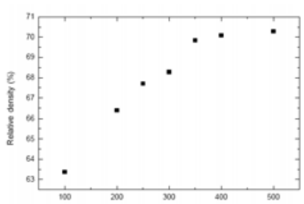




Shaping?

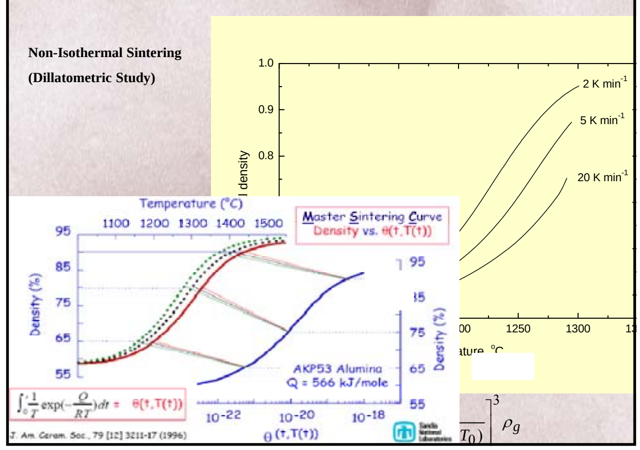


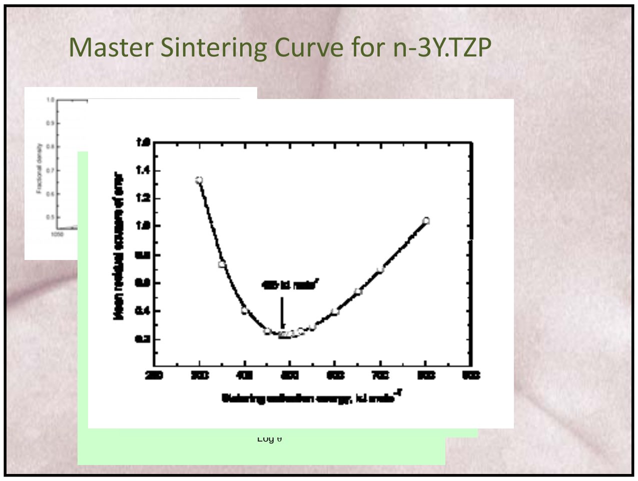


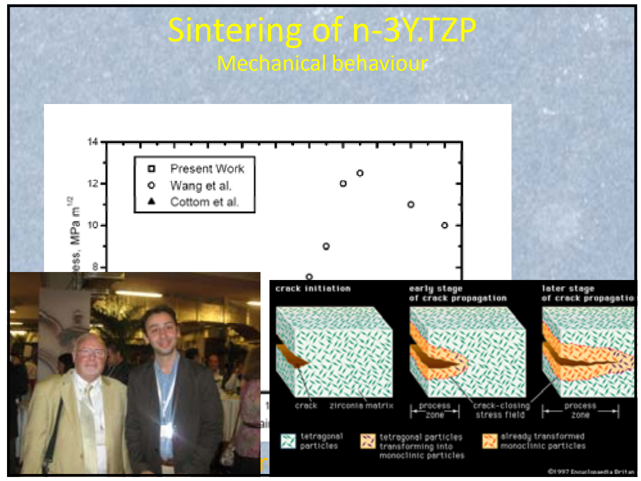


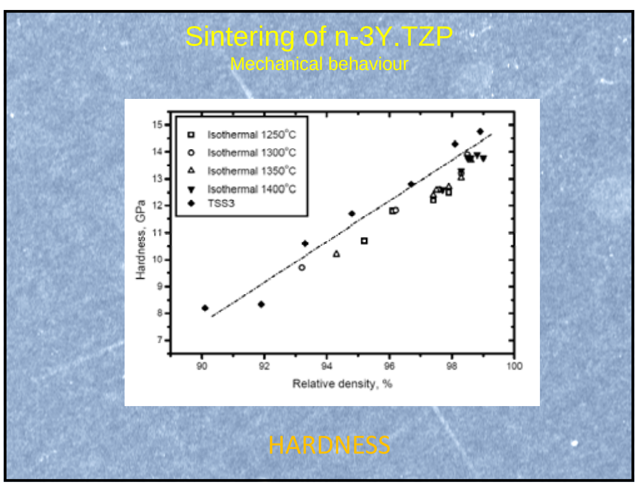
Non-Isothermal Sintering

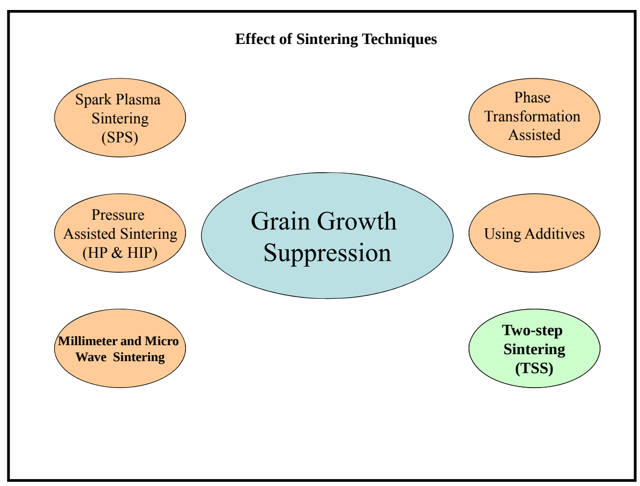
(Dillatometric Study)




Master Sintering Curve for n-3Y.TZP


Sintering of n-3Y.TZP
Mechanical behaviour
Present Work
Wang et al.
Cottom et al.
crack initiation
early stage of crack propagation
crack
zirconia matrix
process zone
crack-closing stress field
tetragonal particles
tetragonal particles transforming into monoclinic particles
already transformed monoclinic particles

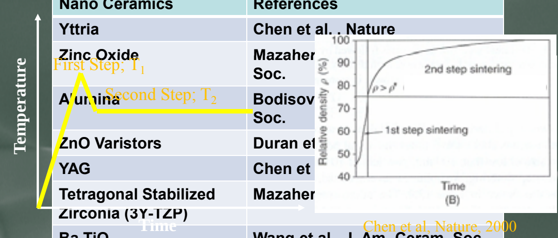

Sintering of n-3Y.TZP
Mechanical behaviour
Isothermal 1250°C
Isothermal 1300°C
Isothermal 1350°C
Isothermal 1400°C
TSS3
Hardness, GPa
Relative density, %
HARDNESS


Effect of Sintering Techniques
Spark Plasma Sintering (SPS)
Phase Transformation Assisted
Pressure Assisted Sintering (HP & HIP)
Grain Growth Suppression
Using Additives
Millimeter and Micro Wave Sintering
Two-step Sintering (TSS)

Two Step Sintering

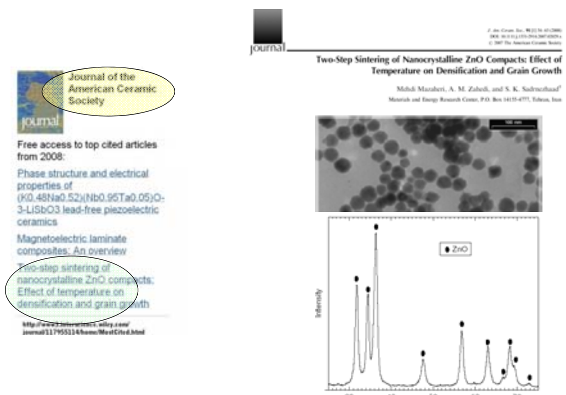
Simple! Physically Powerful!

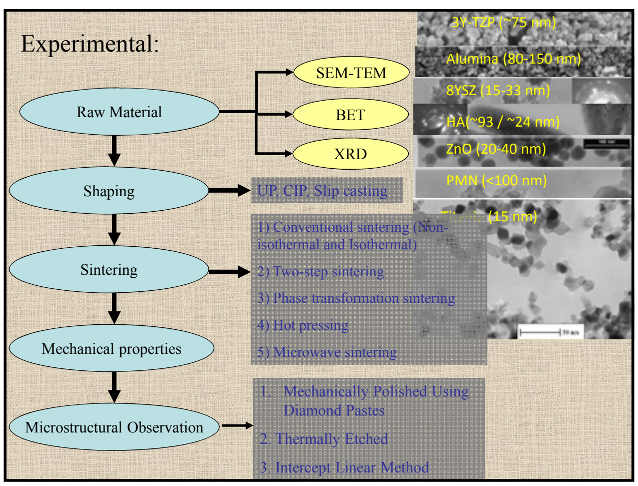
Nano Ceramics	References
Yttria	Chen et al. , Nature
Zinc Oxide	Mazaher… Soc.
Alumina	Bodisov… Soc.
ZnO Varistors	Duran et…
YAG	Chen et…
Tetragonal Stabilized Zirconia (3Y-TZP)	Mazaher…
Ba TiO_3	Wang et al., J. Am. Ceram. Soc.
Titania	Mazaheri et al., Scripta Mat.



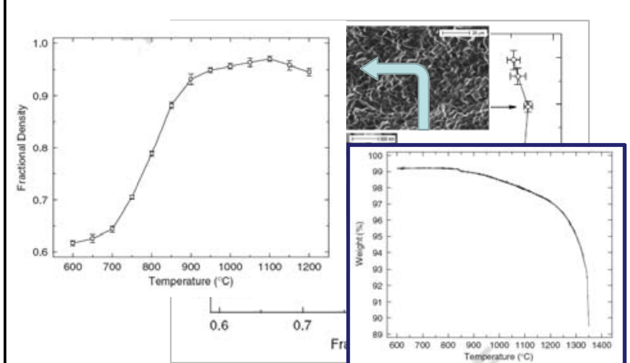
Sintering of n-ZnO

CS-TSS and HP

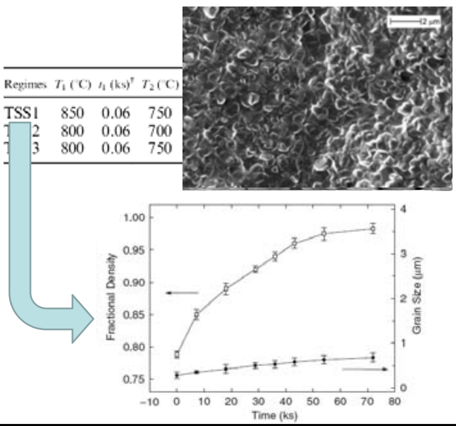




Conventional Sintering of n-ZnO

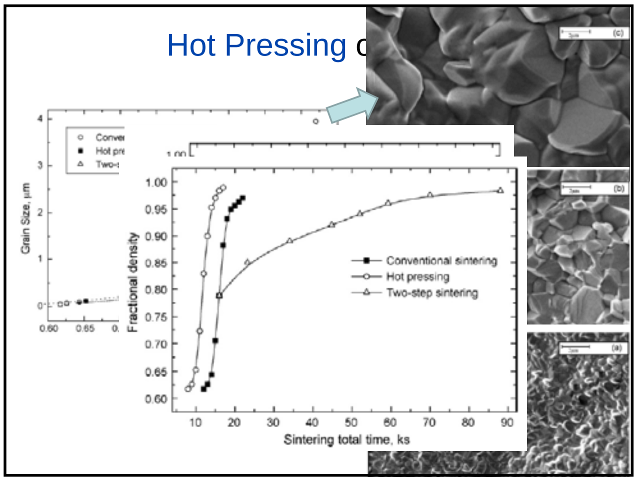


2 Step Sintering of n-ZnO



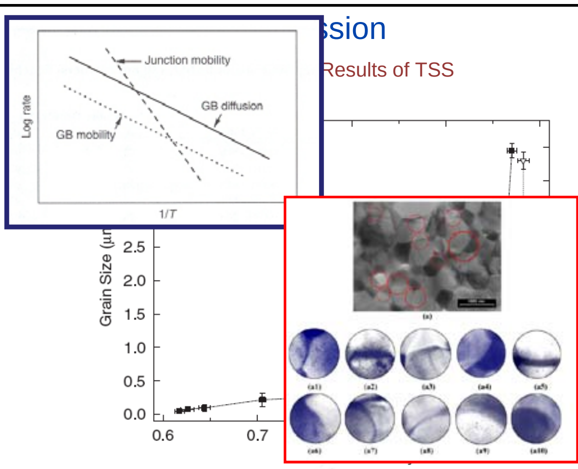
Regimes	T_1 (°C)	t_1 (ks)[†]	T_2 (°C)
TSS1	850	0.06	750
[illegible]2	800	0.06	700
[illegible]3	800	0.06	750

Hot Pressing c



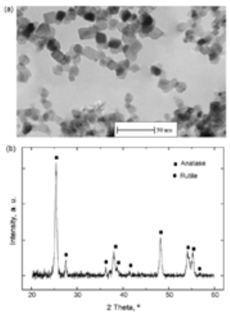
ssion

Results of TSS

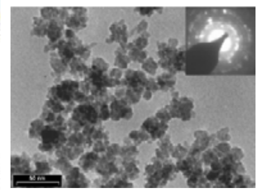


Application?

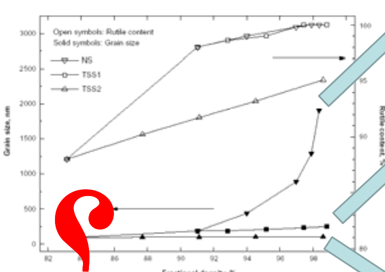
Sintering of n-Titania
CS,TSS and assisted by phase-transformation



Processing of 8YSZ
Sintering methods: CS, TSS and Microwave Sintering
Shaping methods: Uniaxial pressing, Slipcasting

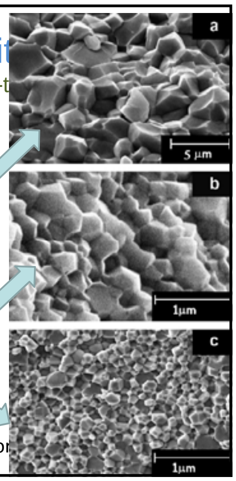


Sintering of n-Ti
CS,TSS and assisted by phase-t

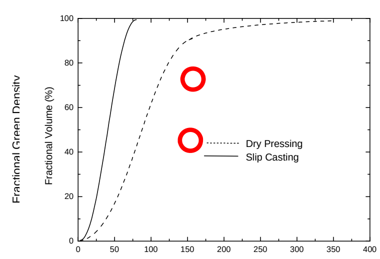


Behavior

K.-N.P. Kumar, K. Keizer, A.J. Burggraaf, T. Okubo, H. Nagamoto, S. Morooka, Nature 358 (1992) 48.

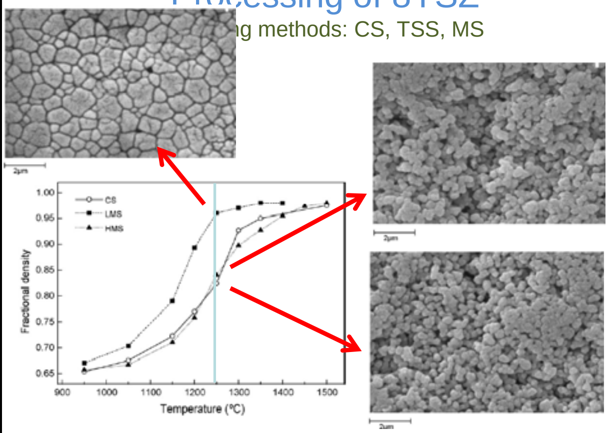


Processing of 8YSZ
Shaping methods: Uniaxial pressing, Slipcasting



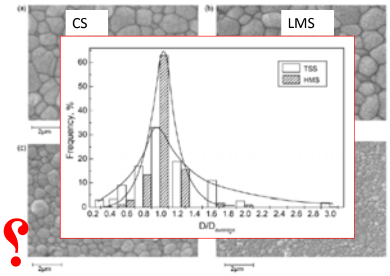
Processing of 8YSZ

ng methods: CS, TSS, MS



Processing of 8YSZ

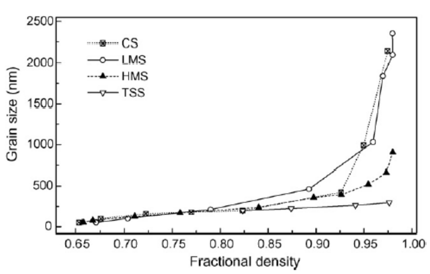
Microstructure and Mechnical behaviour



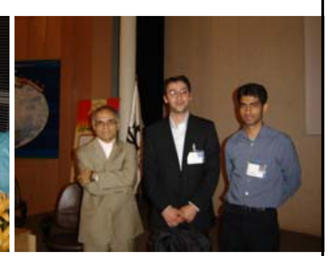
Sintering method	Average grain size (μm)	Fractional density	Hardness (GPa)	Fracture toughness ($MPa\,m^{1/2}$)
CS	2.14	97.5	12.87 ± 0.12	1.61 ± 0.07
LMS	2.35	98	12.97 ± 0.19	1.9 ± 0.09
HMS	0.9	98	13.72 ± 0.22	3.17 ± 0.10
TSS	0.29	97.6	13.51 ± 0.17	3.16 ± 0.06

Processing of 8YSZ

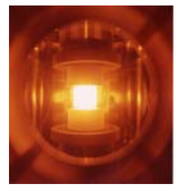
Sintering methods: CS, TSS, MS

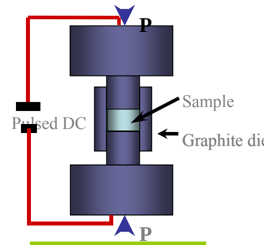


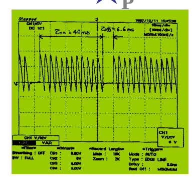
Conclusion 1



Spark plasma sintering







The first SPS unit in Europe, Dr Sinter 2050, installed in 1998

Spark Plasma Sintering

&

Thermo-Mechanical Properties

SPS $\geq$ HP

Pressure effect

For Coble creep based grain boundary sliding

in intermediated stage

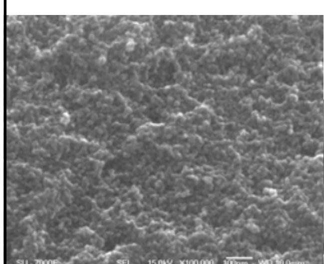
$$\frac{d(-\Delta L/L_0)}{dt} = \frac{95}{2}\left(\frac{D_{gb}\delta_{gb}\Omega}{G^3 kT}\right)\left(P_a\phi + \frac{\gamma_{sv}}{r}\right)$$

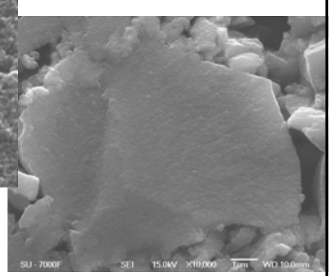
in final stage

$$\frac{d(-\Delta L/L_0)}{dt} = \frac{15}{2}\left(\frac{D_{gb}\delta_{gb}\Omega}{G^3 kT}\right)\left(P_a\phi + \frac{2\gamma_{sv}}{r}\right)$$

D_{gb} : GB diffusion coefficient, δ_{gb} : GB width, Ω : atomic volume, G : grain size, k : Boltzmann constant, T : the absolute temperature, γ_{sv} is the solid-vapour surface energy, r : pore size. p_a : applied stress.

Sintering or packing?



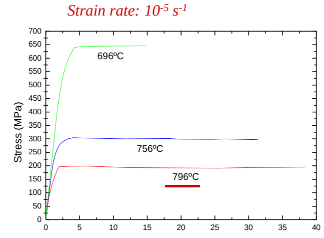


MgO Superplasticity

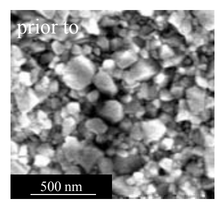
— Grain boundary sliding

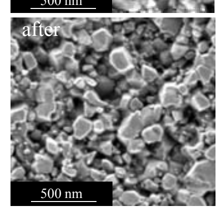
0.3 T_m *vs* 0.5T_m

Strain rate: 10^{-5} s^{-1}

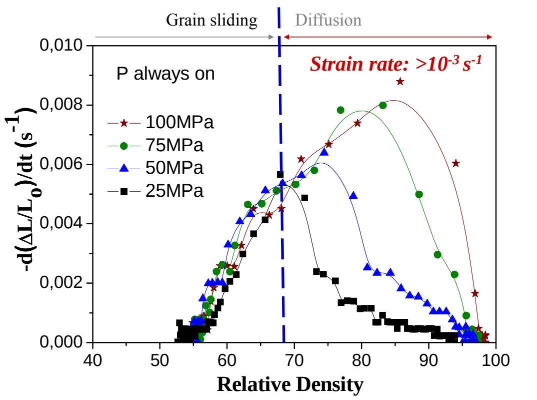


Compressive deformation under constant cross-head speed

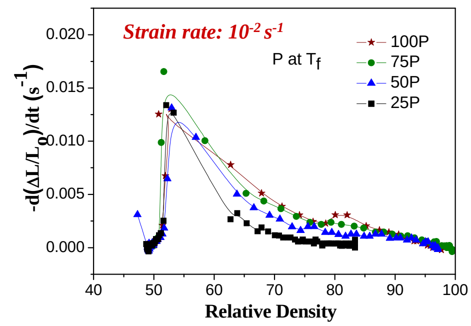




Densification rate



Densification rate: P at T_f



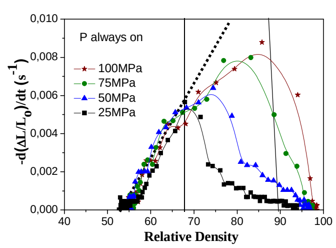
in intermediated stage

$$\frac{d(-\Delta L/L_0)}{dt} = \frac{95}{2}\left(\frac{D_{gb}\delta_{gb}\Omega}{G^3 kT}\right)\left(P_a\phi + \frac{\gamma_{sv}}{r}\right)$$

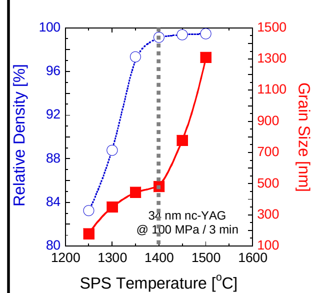
in final stage

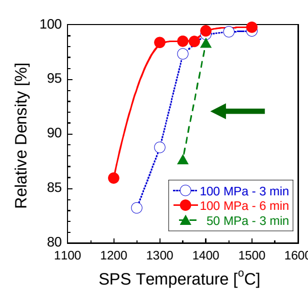
$$\frac{d(-\Delta L/L_0)}{dt} = \frac{15}{2}\left(\frac{D_{gb}\delta_{gb}\Omega}{G^3 kT}\right)\left(P_a\phi + \frac{2\gamma_{sv}}{r}\right)$$

Intermedialte stage, 32%≤ Vp ≤ 10%, no linear relation
Final stage, Vp ≤ 10%, no linear relation



Consolidating YAG under high pressure

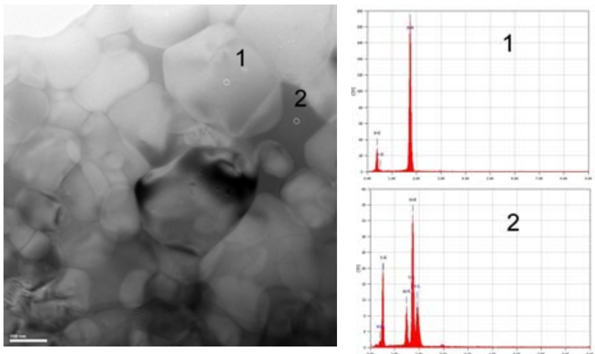




Spherical powder, **34 nm**

J. of Euro Ceram. Soc. (2007) , 27(11), 3331-3337

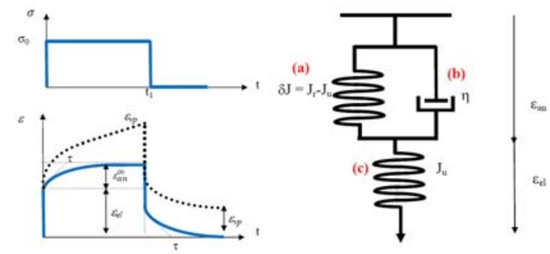
Densification while retarding solution-reprecipitation



Bright-field TEM image, beta-powder, grain size: 76 nm, SPS 1500oC under 50 MPa for 3 min. Note the aggregate feature of the large grains.

Introduction 2- Anelasticity

Anelastic Relaxation



$$\varepsilon_{an} = \varepsilon_{an}^{\infty}\left[\left(1 - \exp\left(-\frac{t}{\tau}\right)\right]\right.$$

$$J_r\sigma + J_u\tau\dot{\sigma} = \varepsilon + \tau\dot{\varepsilon}$$

$$\Delta = \frac{\varepsilon_{an}^{\infty}}{\varepsilon_{el}} = \frac{J_r - J_u}{J_u}$$

Introduction (2)- Ceramics?

Grain refining

Increasing of fracture toughness at room temperature

High temperature mechanical properties
(G.B. sliding accommodated by diffusion or interface reaction mechanisms)

$$\dot{\varepsilon}(\sigma,T) = A\left(\frac{\sigma-\sigma_0}{G}\right)^n\left(\frac{b}{d}\right)^p D$$

Nano-structured ceramics reinforced by nano-particles or fibers

Higher creep resistance
(Ionascu, EPFL Thesis, 2008)

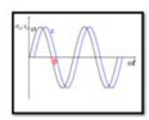
3 times higher fracture toughness
(Zhang et al, Nature Materials, 2003)

Introduction 2- Mechanical spectroscopy

Periodic stress: $\sigma = \sigma_o \exp[i(\omega \cdot t)]$

Strain response: $\varepsilon = \varepsilon_o \exp[i(\omega \cdot t - \Phi)]$

$$\frac{\varepsilon}{\sigma} = J^*(\omega) = J_1(\omega) - iJ_2(\omega)$$



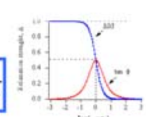
✓Phase lag is due to anelasticity of the material
✓Anelastisity is due to motion of structural defects

Mechanical spectroscopy is applicable for investigations of significant features such as local distortion of lattices (point defect relaxation), dislocation motions and grain-boundary sliding processes

$$J_r\sigma + J_u\tau\dot{\sigma} = \varepsilon + \tau\dot{\varepsilon}$$

$$\tan\phi = \frac{J_2}{J_1} = \Delta\frac{\omega\tau}{1+\omega^2\tau^2} \qquad \frac{\delta J}{J} = \frac{\Delta}{1+\omega^2\tau^2}$$

Debye equations

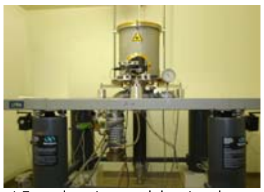


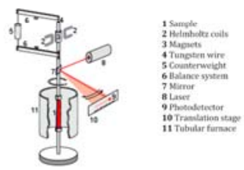
Introduction 2- Mechanical spectroscopy

High tem...

Mechanical spectroscopy

...phase

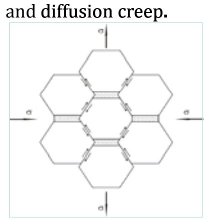




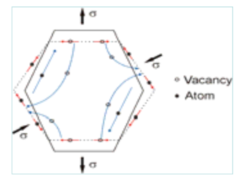
* Forced torsion pendulum in sub-resonant mode
* Temperature: RT- 1600 K
* Frequency: 10^{-4} and 10 Hz
* Vacuum: 10^{-3} Pa

Introduction (3) – Application of M.S. in ceramics

High-temperature plasticity of **fine-grained ceramics** **proceeds by** mutually accommodating **grain boundary sliding** and **diffusion creep.**

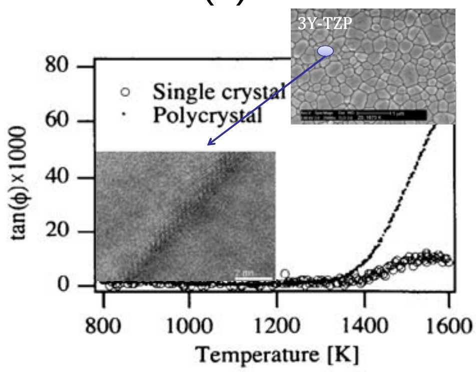


Grain boundary sliding creates voids or overlaps that have to be accommodated by diffusion.



Diffusion processes are:
- Nabarro-Herring creep
- Coble creep

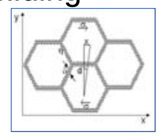
First results (2) – 3Y.TZP

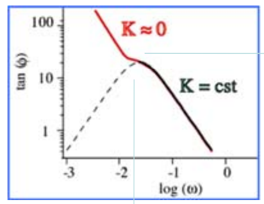


Donzel et al. Acta Mater. 2000

Lakki's model for GB sliding

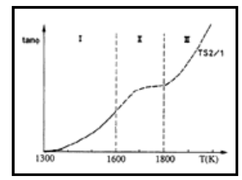
$$\tan(\varphi) = \frac{G}{d}\frac{\omega\frac{\eta}{\delta}}{\left(\frac{KG}{d}+K^2\right)+\left(\omega\frac{\eta}{\delta}\right)^2}$$



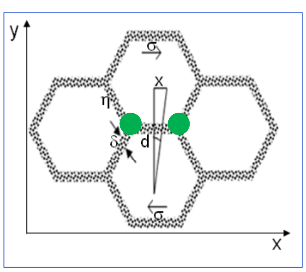


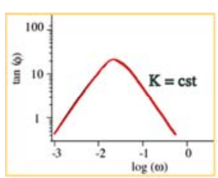
$$\tan(\phi)\big|_{\omega=\omega_p} = \frac{G}{2d\sqrt{\frac{KG}{d}+K^2}}$$

$$\omega_p = \frac{\delta}{\eta}\sqrt{\frac{KG}{d}+K^2}$$



Theoretical model for GB sliding





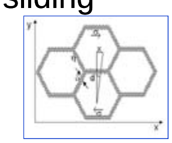
$$\sigma = \sigma_0\cos(\omega t)$$

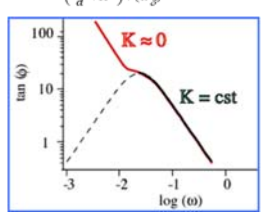
$$\varepsilon = \varepsilon_0\cos(\omega t - \varphi)$$

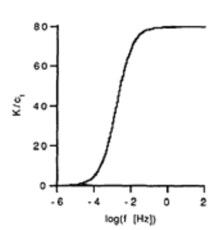
$$\tan(\varphi) = \frac{G}{d}\frac{\omega\frac{\eta}{\delta}}{\left(\frac{KG}{d}+K^2\right)+\left(\omega\frac{\eta}{\delta}\right)^2}$$

Lakki's model for GB sliding

$$\tan(\varphi) = \frac{G}{d}\frac{\omega\frac{\eta}{\delta}}{\left(\frac{KG}{d}+K^2\right)+\left(\omega\frac{\eta}{\delta}\right)^2}$$







$$K(\omega) = c.\frac{\sigma}{\varepsilon_{el}+\varepsilon_{pl}(t)} = c.\frac{\sigma}{\frac{\sigma}{G}+A\frac{\sigma^2}{d}\exp\left(\frac{E_{act}}{kT}\right).t}$$

What is the aim of this work?

Silicon nitride based ceramics (SiAlON)

Yttria Stabilized Zirconia (3Y.TZP)

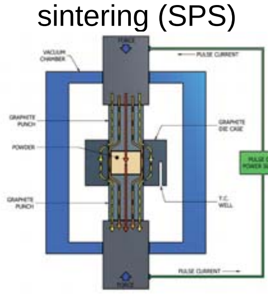
Materials

Hot Press & Spark Plasma Sintering

2073 K, 35 MPa and 4 h

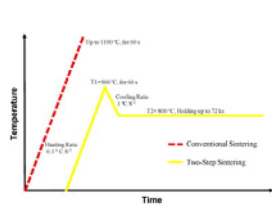
- Ca-SiAlON (Si_3N_4, AlN, CaH_2)
  - CN04, CN08, CN16
- Ca-SiAlON (Si_3N_4, AlN, CaO)
  - CO04, CO14
  - $Ca_xSi_{12-3x}Al_{3x}O_xN_{16-x}$, x=0.4, 1.4
- Y-SiAlON (Si_3N_4, AlN, Y_2O_3/YN)
  - YO04, YN04
- Yb-SiAlON (Si_3N_4, AlN, Yb_2O_3/YbN
  - YbO04, YbN04

Spark plasma sintering (SPS)



SPS apparatus in Lyon

Two-step sinteirng



Materials

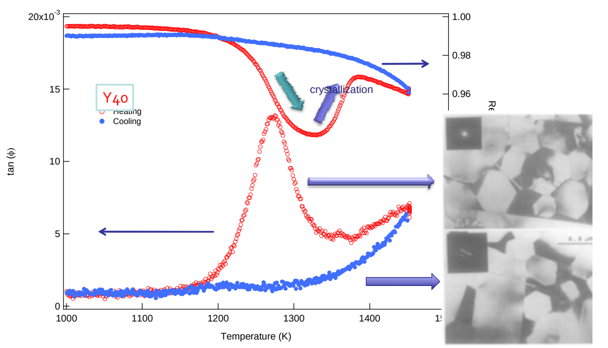
Hot Press & **Spark Plasma Sintering**

1773 K, 50 MPa and only 3 min

↓

Si_3N_4 + 6wt% Al_2O_3 + 6wt% Y_2O_3

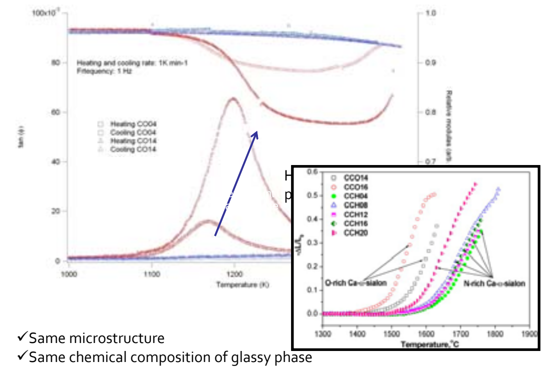
Si_3N_4 based ceramics



Lakki et al, Acta. Mater., 1995.

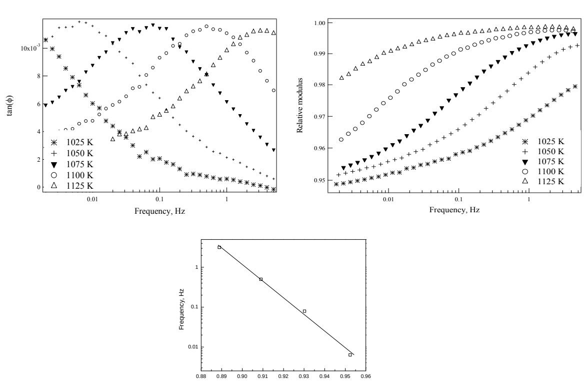
Si_3N_4 based ceramics

(CO04 and CO14)

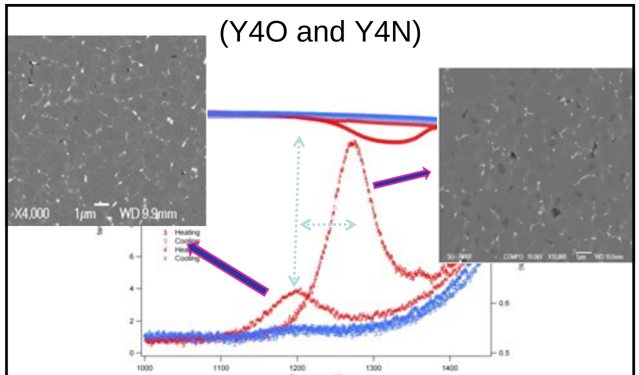


✓Same microstructure
✓Same chemical composition of glassy phase

Si_3N_4 based ceramics



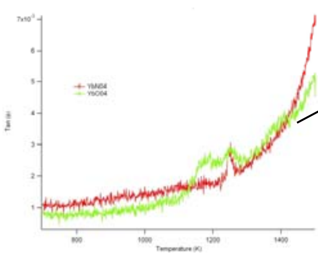
(Y4O and Y4N)

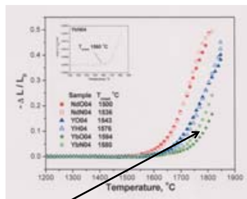


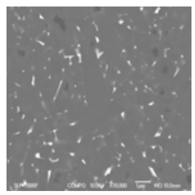
1. Equiaxed grains (as same!)
2. Grain size (as same!)

Results (Yb4O and Yb4N)

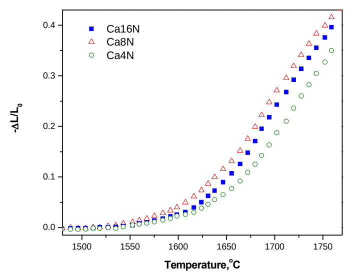
YbOo4 (Si_3N_4 + AlN + Yb_2O_3)
YbNo4 (Si_3N_4 + AlN + YbN)



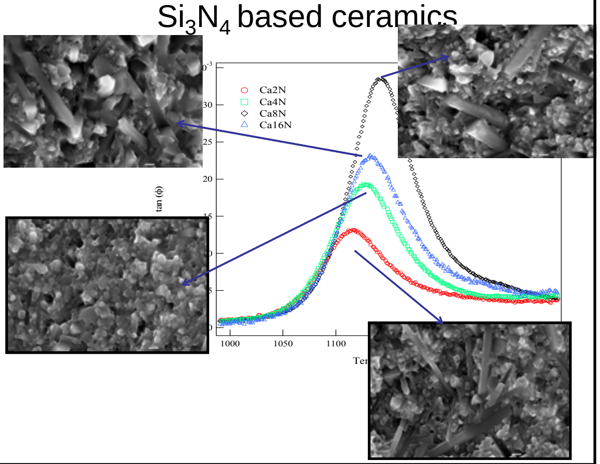




Si_3N_4 based ceramics



Si_3N_4 based ceramics

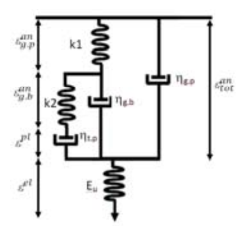


Si_3N_4 based ceramics

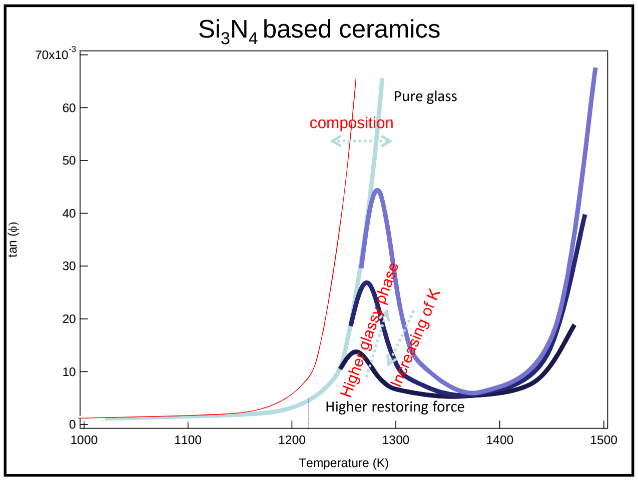
- Real Si_3N_4 system

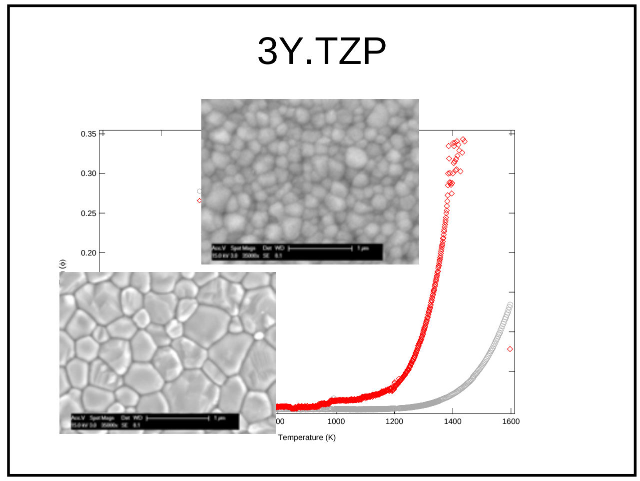
$$\varepsilon^{tot} = \varepsilon^{el} + (1-f)\,\varepsilon^{an}_{g.b} + f\,\varepsilon^{an}_{g.p}$$

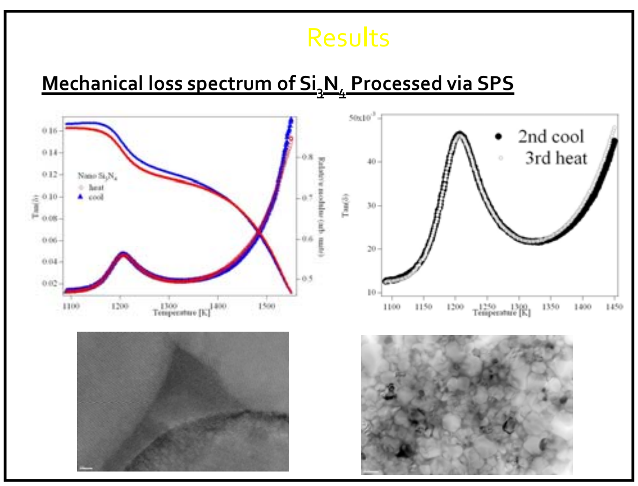
$$\tan(\varphi) = \frac{f}{1-f}\cdot\frac{1}{J_{u\,k}}\cdot\frac{\omega.\eta/k}{1+(\omega\frac{\eta}{k})^2}$$

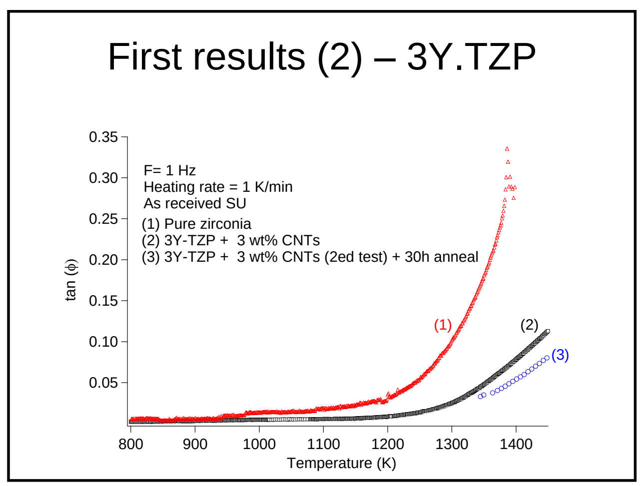


To be published in Acta Materialia

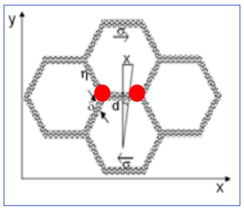

Si3N4 based ceramics
70x10-3
60
50
40
30
20
10
0
tan (φ)
Pure glass
composition
Higher glassy phase
Increasing of K
Higher restoring force
1000
1100
1200
1300
1400
1500
Temperature (K)

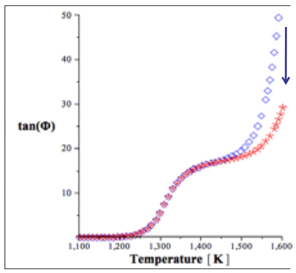

3Y.TZP
0.35
0.30
0.25
0.20
1000
1200
1400
1600
Temperature (K)


Results
Mechanical loss spectrum of Si3N4 Processed via SPS
2nd cool
3rd heat


First results (2) – 3Y.TZP
F= 1 Hz
Heating rate = 1 K/min
As received SU
(1) Pure zirconia
(2) 3Y-TZP + 3 wt% CNTs
(3) 3Y-TZP + 3 wt% CNTs (2ed test) + 30h anneal
0.35
0.30
0.25
0.20
0.15
0.10
0.05
tan (φ)
(1)
(2)
(3)
800
900
1000
1100
1200
1300
1400
Temperature (K)

3Y.TZP



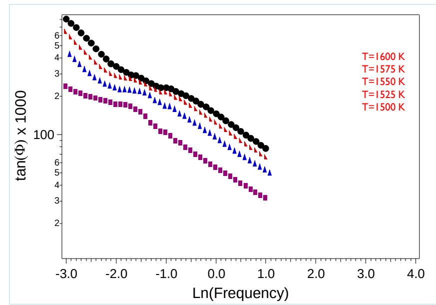


$\sigma = \sigma_o \sin(\omega t)$

$\varepsilon = \varepsilon_o \sin(\omega t - \Phi)$

$$\tan(\Phi) = \frac{G}{d}\frac{1}{K}\left(\frac{\omega\tau}{1+\omega^2\tau^2}\right)$$

Power law equation of creep



$$\delta(\log(\omega)) = -\frac{\Delta H_{act}}{R \cdot ln(10)}\delta\left(\frac{1}{T}\right) - \delta(\log(\tau_o))$$

Power law equation of creep

$$\dot{\varepsilon}(\sigma,T) = A\left(\frac{\sigma}{G}\right)^n\left(\frac{b}{d}\right)^p \exp\left(-\frac{\Delta H_{act}}{RT}\right)$$

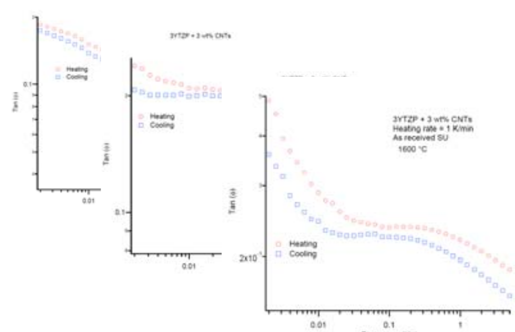
A - material constant
σ – constant applied stress
G – shear modulus
b – Burger vector
d – grain size
ΔH_{act} – activation enthalpy (characteristic for underlying mechanism)
R – universal gas constant

$$\tan(\Phi) = A'\frac{G\sigma^{n-1}}{\omega d^p}\exp\left(-\frac{\Delta H_{act}}{RT}\right)$$

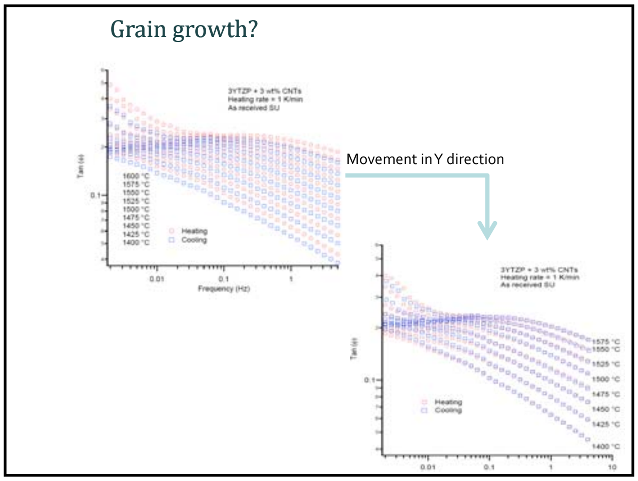
$$\log\{\tan(\Phi)\} + p[\dots] + (1-[\dots])\log(\sigma) = -\frac{\Delta H_{act}}{RT\ln(10)} + \log(\omega) + C$$

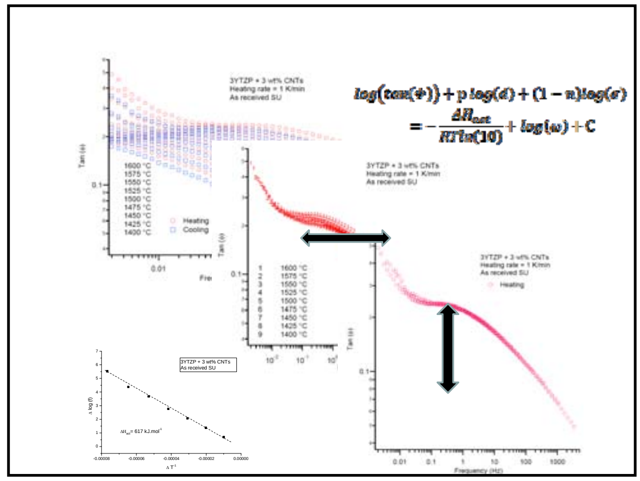
$$\delta(\log(\omega)) = -\frac{\Delta H_{act}}{R \cdot ln(10)}\delta\left(\frac{1}{T}\right) - \delta(\log(\tau_o))$$

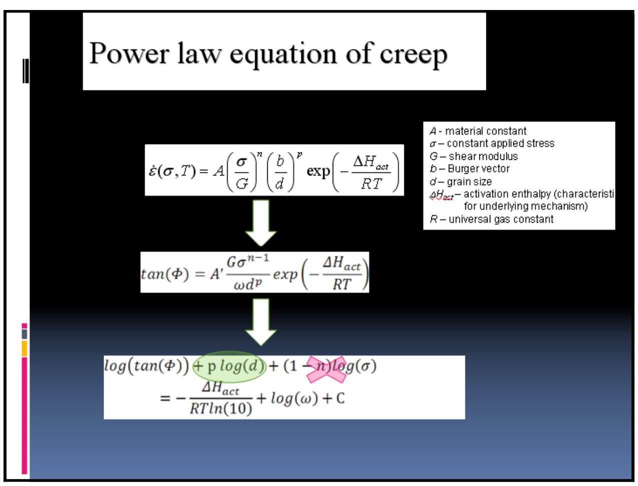
Grain growth?

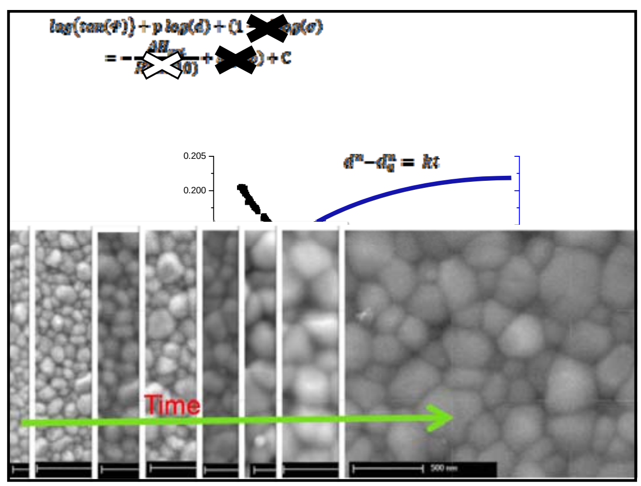


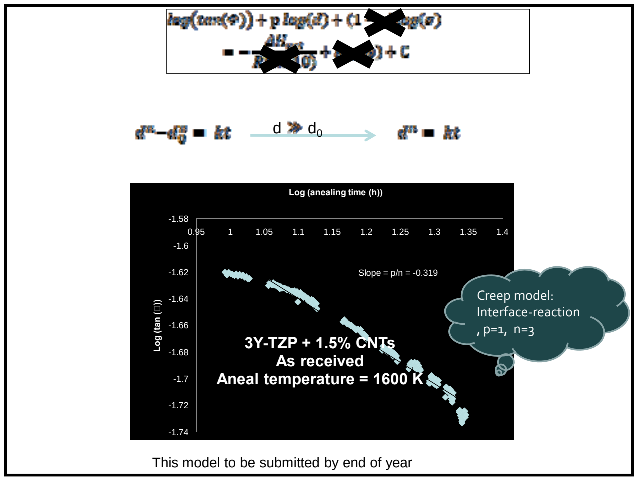
$\tan(\Phi) = \tan\left(\Phi\left[\log(\dots\omega) + \frac{\Delta H_{act}}{R \cdot ln(10)}\frac{1}{T} + \log(\tau_o)\right]\right)$

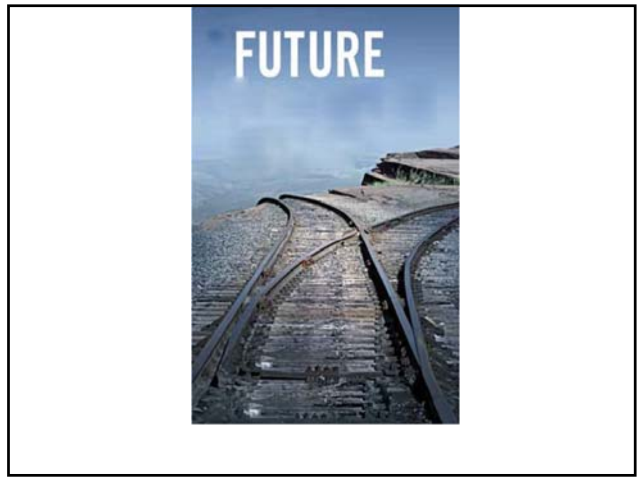

Grain growth?
Movement in Y direction

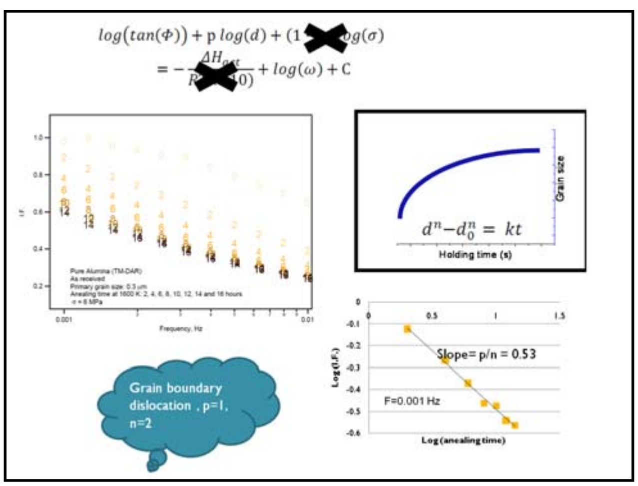

$log(tan(\Phi)) + p\,log(d) + (1-n)log(\sigma)$
$= -\frac{\Delta H_{act}}{RTln(10)} + log(\omega) + C$

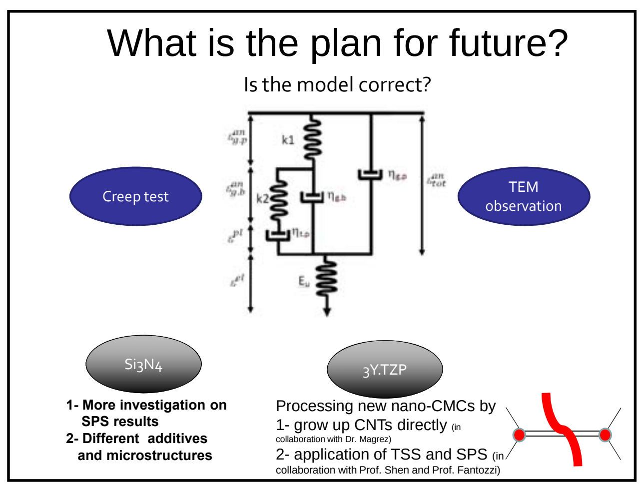

Power law equation of creep
$\dot{\varepsilon}(\sigma,T) = A\left(\frac{\sigma}{G}\right)^n\left(\frac{b}{d}\right)^p \exp\left(-\frac{\Delta H_{act}}{RT}\right)$
A - material constant
σ – constant applied stress
G – shear modulus
b – Burger vector
d – grain size
ΔHact – activation enthalpy (characteristi for underlying mechanism)
R – universal gas constant
$tan(\Phi) = A'\frac{G\sigma^{n-1}}{\omega d^p}exp\left(-\frac{\Delta H_{act}}{RT}\right)$
$log(tan(\Phi)) + p\,log(d) + (1-n)log(\sigma)$
$= -\frac{\Delta H_{act}}{RTln(10)} + log(\omega) + C$


$d^n - d_0^n = kt$
Time


d ≫ d_0
Log (anealing time (h))
Slope = p/n = -0.319
Creep model: Interface-reaction , p=1, n=3
3Y-TZP + 1.5% CNTs
As received
Aneal temperature = 1600 K
This model to be submitted by end of year


FUTURE


$d^n - d_0^n = kt$
Holding time (s)
Grain size
Frequency, Hz
Slope= p/n = 0.53
F=0.001 Hz
Log (anealing time)
Grain boundary dislocation , p=1, n=2


What is the plan for future?
Is the model correct?
Creep test
TEM observation
Si3N4
3Y.TZP
1- More investigation on SPS results
2- Different additives and microstructures
Processing new nano-CMCs by
1- grow up CNTs directly (in collaboration with Dr. Magrez)
2- application of TSS and SPS (in collaboration with Prof. Shen and Prof. Fantozzi)

Acknowledgment

Prof. R. Schaller
Dr. Daniele Mari
Prof. Z. Shen
Prof. G. Fantozzi
Dr. C. Yanbing