African school of fundamental physics and applications, Dakar 2014

Introductory talk

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Outline

- Background
- PhD
- International conferences attended
- Some recent Publications...

Background

Trento- Dakar
(Masters- Physics)

Trento-Italy
(PhD- Materials Science)

Lecturer
Univ. CAD
Dept. Physics

Spark Plasma Sintering (SPS)

- -Fast heating rate
- -Short isothermal holding
- -"Low" temperature
- -Application of pressure

Low heat input

Sintering of nanostructured powders with limited grain growth

Nanostructured powder

- High resistance to plastic deformation
- Large density of structural defects

How do they affect densification and sintering in a pressure-assisted sintering process ?

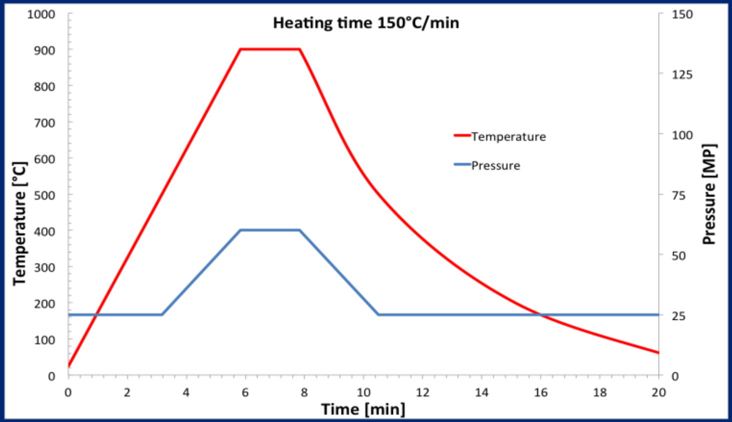
PhD materials synthesis …

STARTING MATERIAL

commercial water atomized Cu powder
purity of 99,6%
particle size <100μm
0.2% of oxygen

CRYOMILLING PARAMETERS

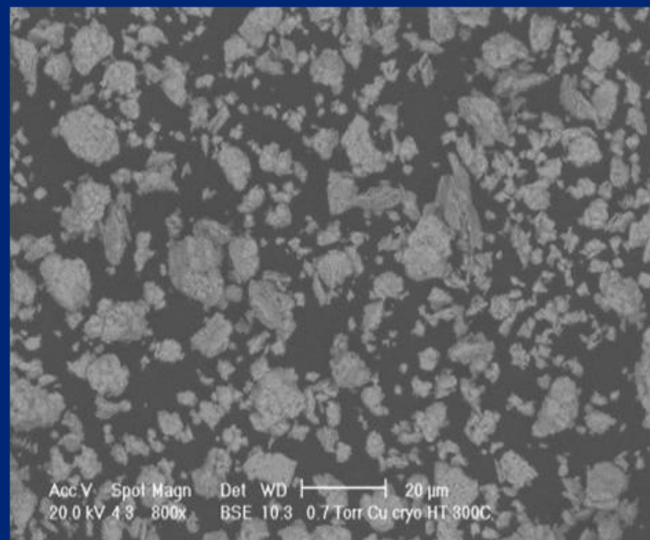
Milling time:	8 hours
Milling rate :	300 rpm
Spheres :	6 mm ϕ stainless steel balls
Ball-to-powder ratio:	30:1

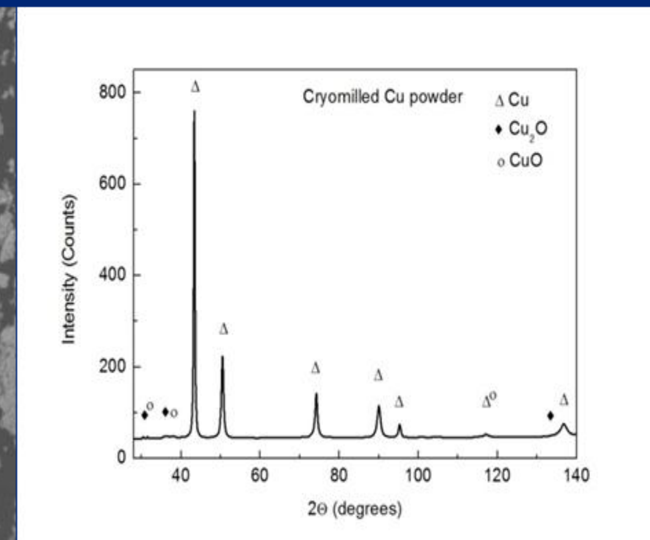


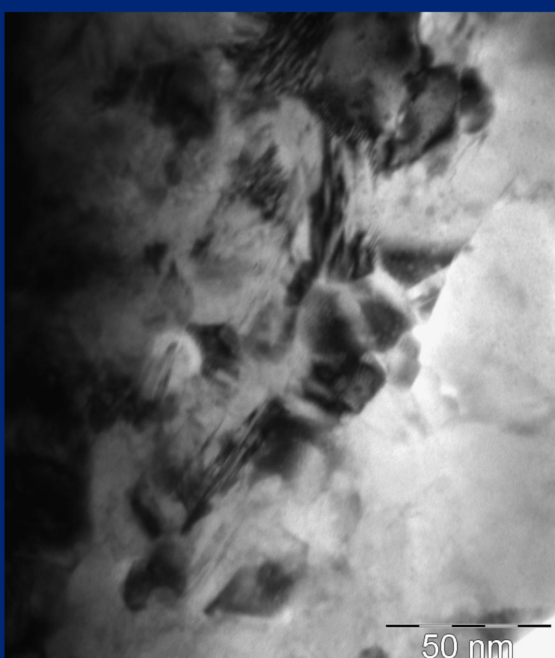
SPARK PLASMA SINTERING PARAMETERS:

Starting pressure	up to 25 MPa
Final pressure	up to 60 MPa
Heating rate	**50°C/min**
	100°C/min
	150°C/min
Sintering temperature	up to 900°C

The synthesized materials characteristics….







D (nm)	ρ_d ($10^{16}m^{-2}$)	%CuO	%Cu_2O	O (%)	N (%)
17 ± 2	6,26 ± 0,04	2,0 ± 0,4	1,8 ± 0,3	1,2	0,2

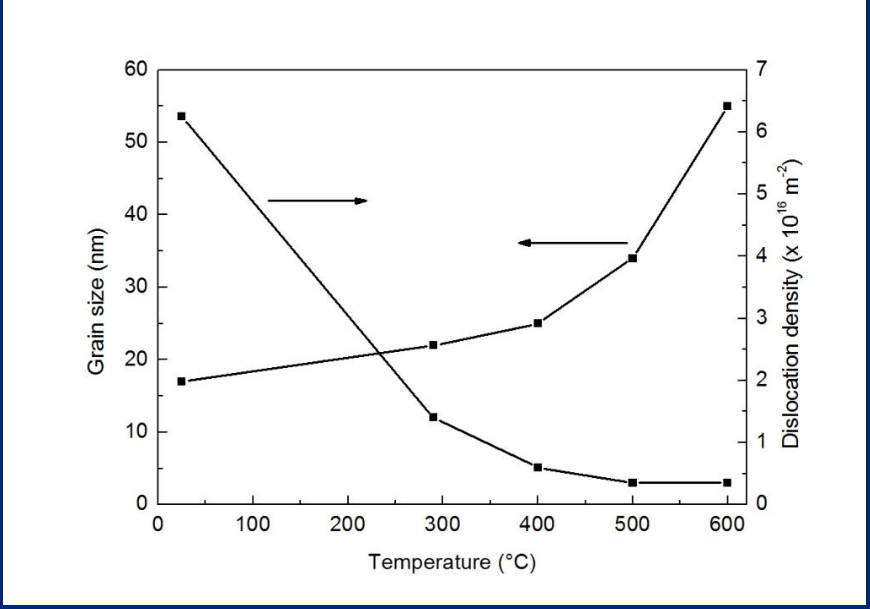
Very fine and highly strained structure

Influence of dislocations on thermal stability

	Mean grain size (nm)	Dislocation density (x $10^{16}m^{-2}$)
As-milled	17	6,25
290°C	22	1,40
400°C	25	0,60
500°C	34	0,35
600°C	55	0,35

Tersid tubular high vacuum furnace (10^{-5} mbar)

XRD data obtained using PM2K Program



Thermal Stability of The Cryomilled Copper

$$\tau_d = 3.3 \frac{\phi \gamma_{gb}}{D}$$

$$\tau_s = \frac{G b \rho^{1/2}}{8\pi(1-\nu)}$$

$$\tau_z = 0.5 \frac{f_{particles} D \gamma_{gb}}{r^2_{particles}}$$

	τ_d (x 10^7 J/m^2)	τ_s (x 10^7 J/m^2)	τ_z (x 10^7 J/m^2)
As-milled	**5,63**	**19**	**0,023**

$$\tau_s >> \tau_d$$

Acta Materialia 58 (2010) 963–966

Spark Plasma Sintering (SPS) Mechanisms

Mechanisms

1

Song model: surface overheating

2

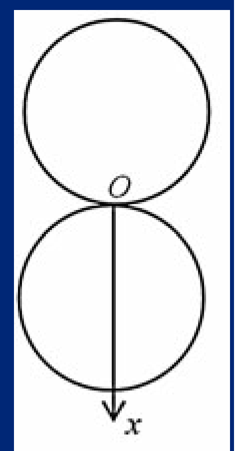
Effect of Nanostructure

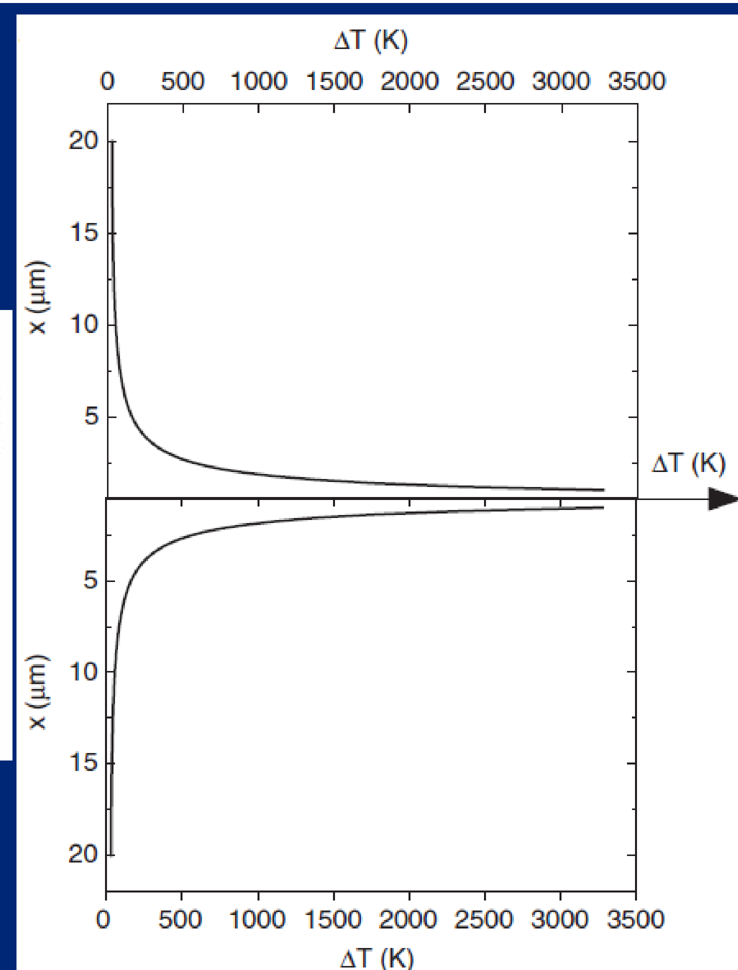
SPS Mechanisms: Song Model

$$\Delta T = \frac{16}{\pi^2}\frac{I_p^2 \rho \Delta t}{C_v \rho_m}\left[\frac{1}{r^2-(r-x)^2}\right]^2$$

$$I_p = \frac{4r^2}{\phi^2} I_S$$

ρ = resistivity (Ω.m)
ρ_m = theoretical density (g/cm^3)
C_v = specific heat ($JK^{-1}mol^{-1}$)
Δt = duration of the pulse
Is = current passing through the sample
I_p = current passing through two particles
r = particle size
ϕ = inner diameter of the die

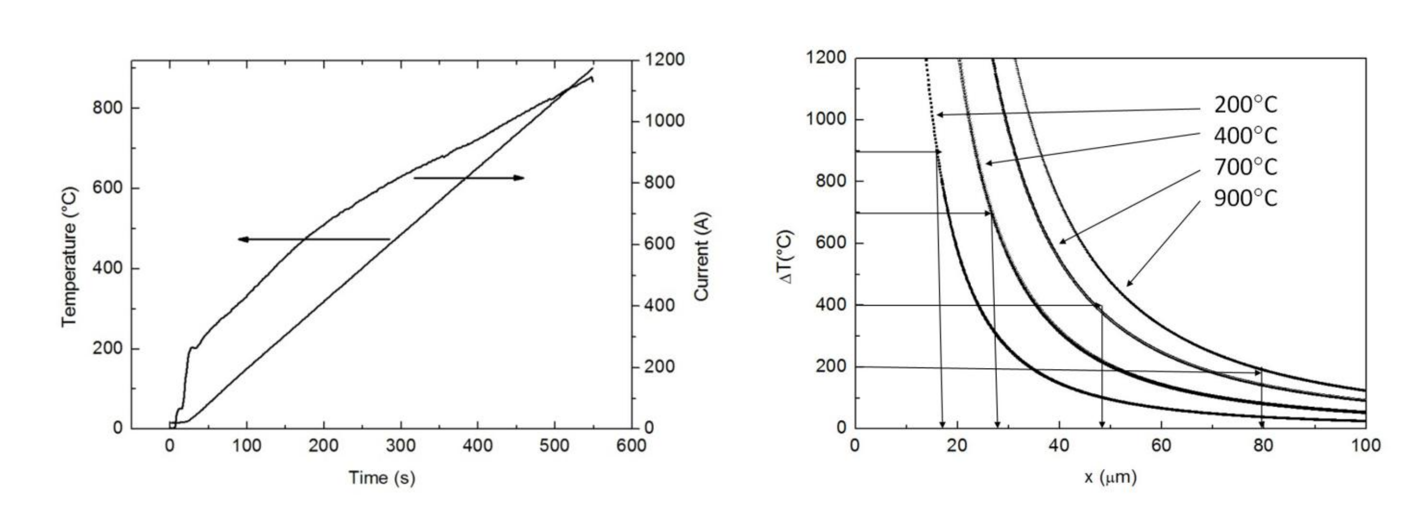




J. Am. Ceram. Soc. 89(2) (2006) 494-500

SPS Mechanisms: Song model

Particle's diameter: 1-3 mm
Pressure: 6 MPa
Specimen dimensions:
- **10 mm height**
- **20 mm diameter**

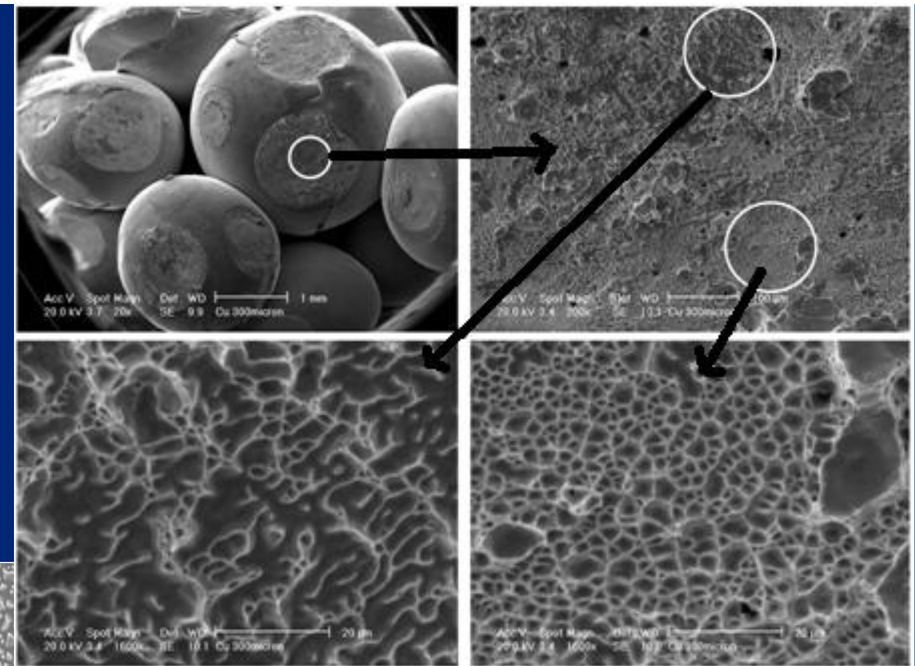


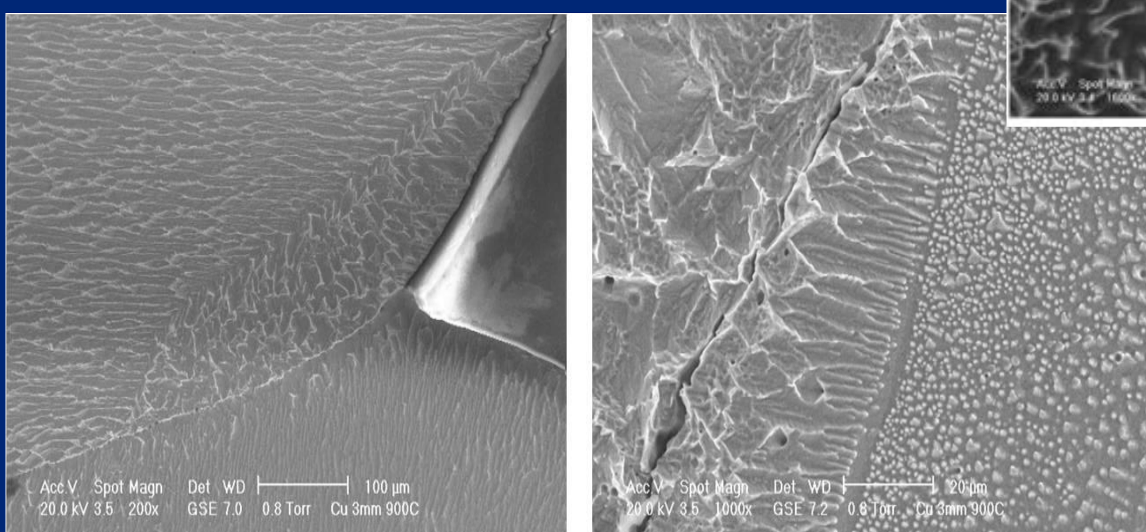
SPS Mechanisms: Song model

two different morphologies:

1. **one cellular with only a few small dimples in the intercellular regions (bottom-left side): weak bonding**

2. **another fully dimpled (bottom-right): ductile fracture**





- Coarser and differently oriented (50-100 µm layer) (right side)

- Equiaxed grains (left side)
Evidence of solidification under Large undercooling

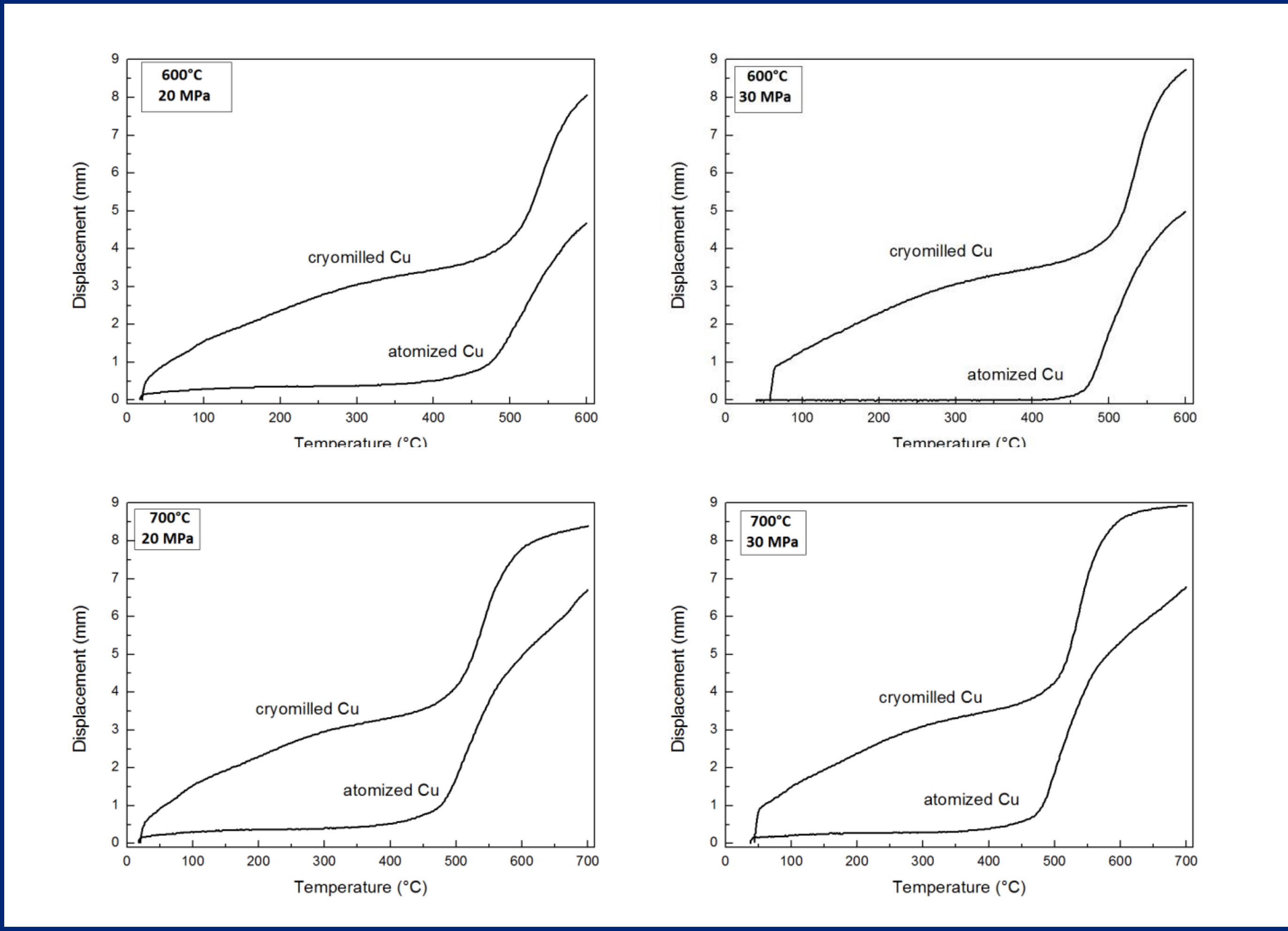
SPS Mechanisms:
Effect on nanostructure on densification

- Temperature:
  600 & 700°C
- Pressure:
  20 & 30 MPa

Displacement curve

↓

Densification



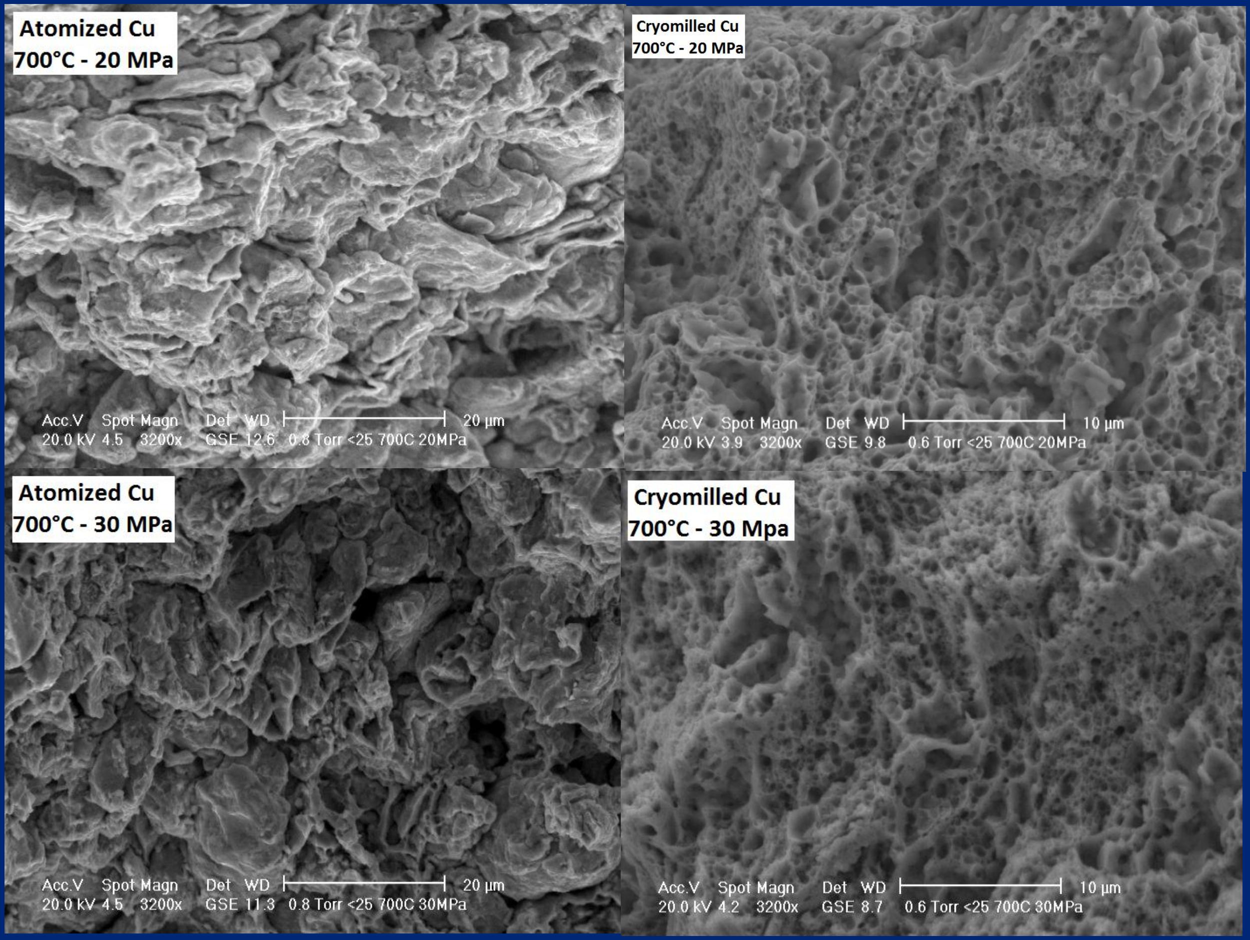
SPS Mechanisms: Effect on nanostructure on sintering

- Temperature: 700°C
- Pressure: 20 & 30 MPa

Fracture Surface

↓

Sintering



SPS Mechanisms: Summary

Atomized powder:

1) rearrangment 2) localized deformation 3) bulk deformation 4) sintering

Nanostructured powder:

1) rearrangment 2) sintering 3) deformation

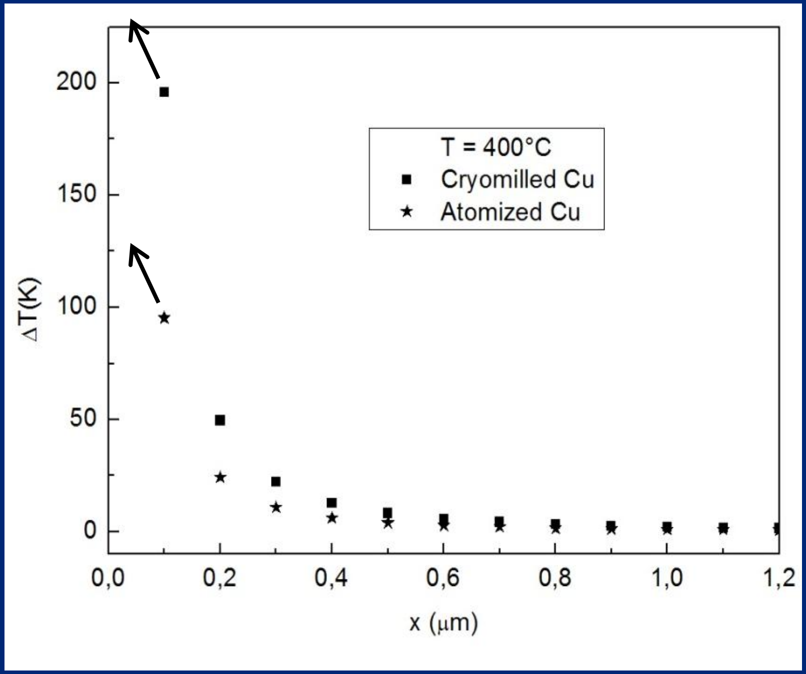
SPS Mechanisms:
Effect on nanostructure on sintering (WHY?)

Nanoparticles have higher **surface energy.**

Same particle size

Surface overheating

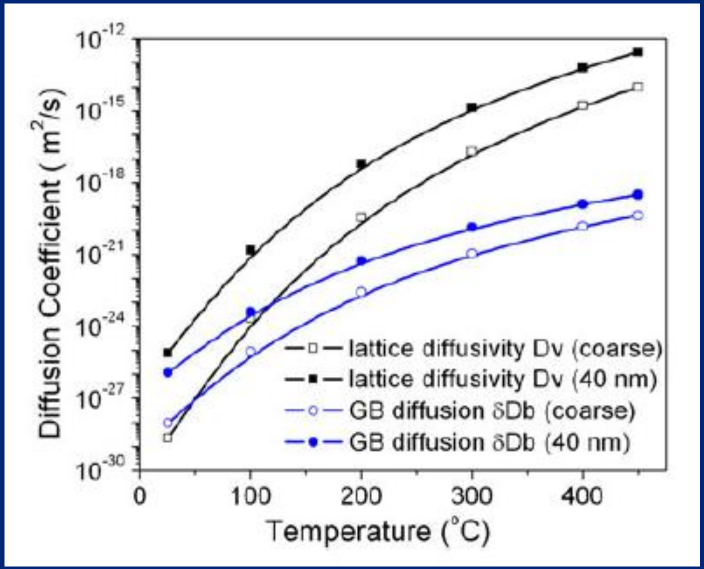
Small differencs



Nanostructure:
- increases resistivity (300%)
- increases specific heat (16%)

SPS Mechanisms:
Effect on nanostructure on sintering

Within the overheated layer **mass transport mechanisms** are activated by the peculiar characteristics of the nanostructure:
- small grain size;
- large density of dislocations



The role of dislocations on volume diffusivity

Dislocation pipe diffusion
$D_p = 10^5\text{-}10^6 D_v$

P. Shewmon, Diffusion in Solids, 2nd edition, 1989, ed. The Minerals, Metals and Materials Society, Warrendale (PA), pp. 202-205

$$D_{eff} = D_v \left(1 + g \left(D_p/D_v\right)\right)$$

g = the fraction of atoms in the pipe
a = pipe radius = 0.5 nm
ρ_d = dislocation density

$$g = a^2 \rho_d$$

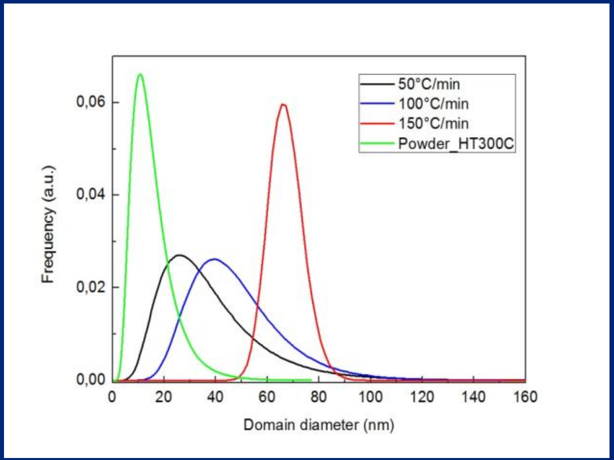
$\rho_d = 6.26 \times 10^{16}\ m^{-2}$ → $g = 0.01$

$\mathbf{D_{eff} = 10^2 D_v}$

Mechanical properties:
Effect of Heating Rate and Pressure on Grain Size Distribution Applying….

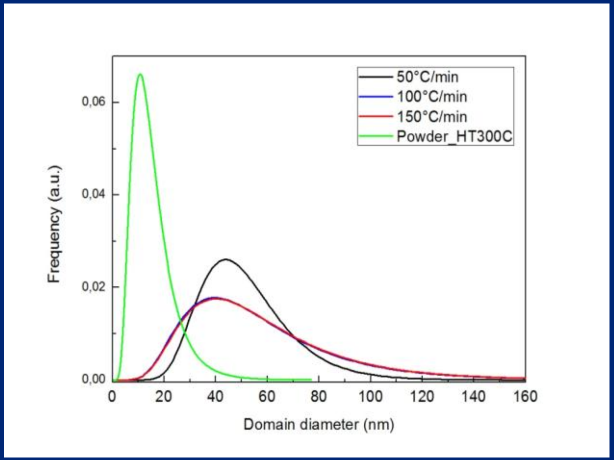
only P_i

Heating rate (°C/min)	Mean Grain Size, D (nm)	ρ_d ($x10^{14}m^{-2}$)
50	38	4,26(1,79)
100	48	6,37(2,82)
150	67	3,99(1,86)

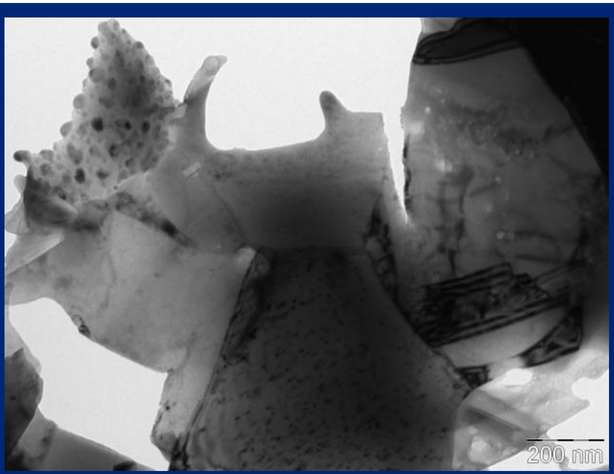


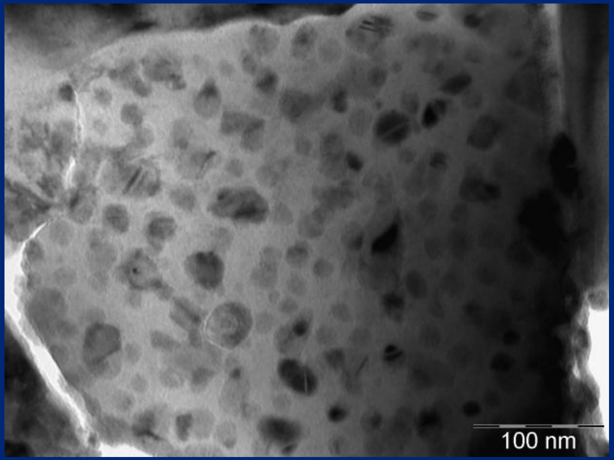
P_i & P_f

Heating rate (°C/min)	Mean grain size, D (nm)	Dislocation density (10^{15} m^{-2})
50	52	2.78 (1.50)
100	58	1.84 (0.61)
150	58	2.44 (1.33)



Effect of Heating Rate on the Size Distribution
Heating rate 50°C/min

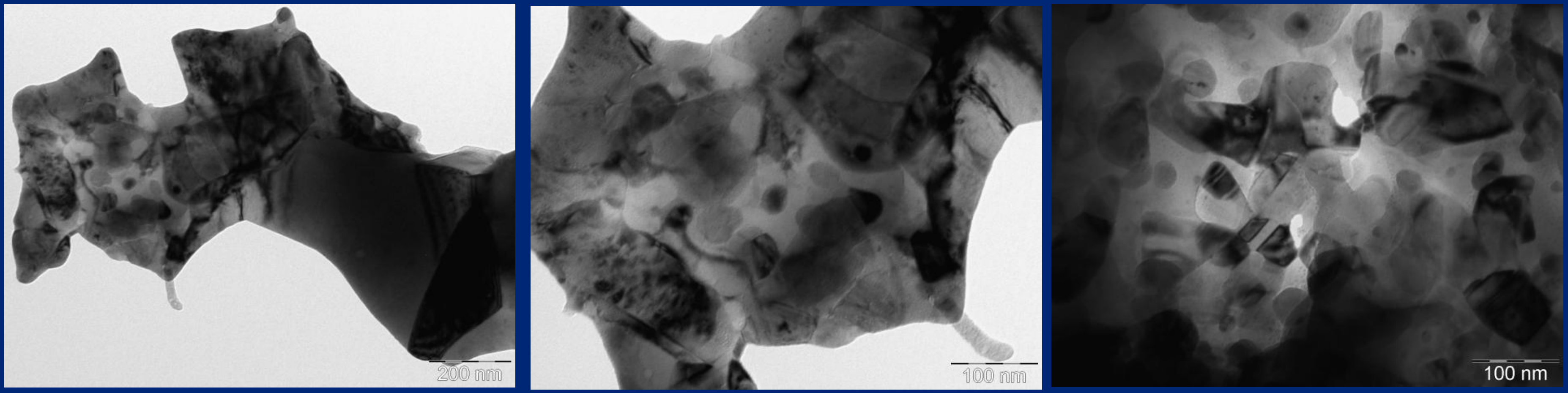




Broad distribution of grain size with defects

The temperature reached in the core of the particle leads to a very slight grain growth (grain size in the starting powder was 22 nm)

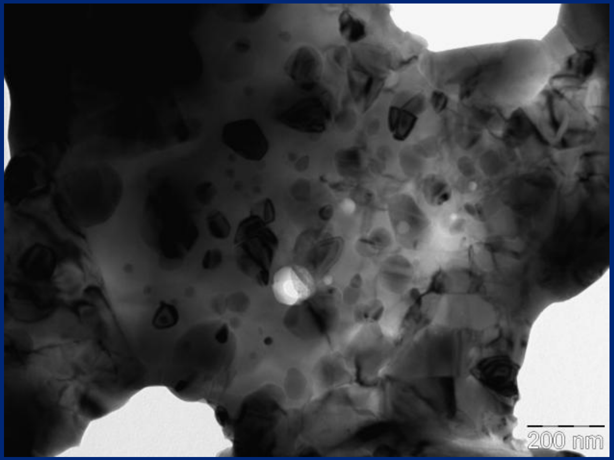
Effect of Heating Rate on the Size Distribution
Heating rate 100°C/min

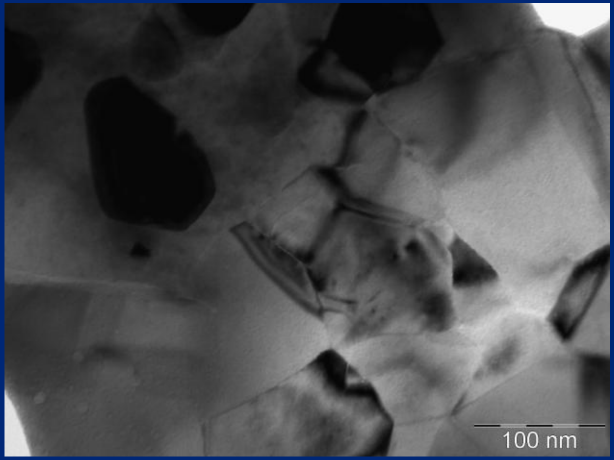


Tendency to the formation of a bimodal distribution of grain size with ultrafine and micrometric grains

- Coarsened grains are defect free and very clean
- In the ultrafine areas the grain size is about 100 nm

Effect of Heating Rate on the Size Distribution
Heating rate 150°C/min



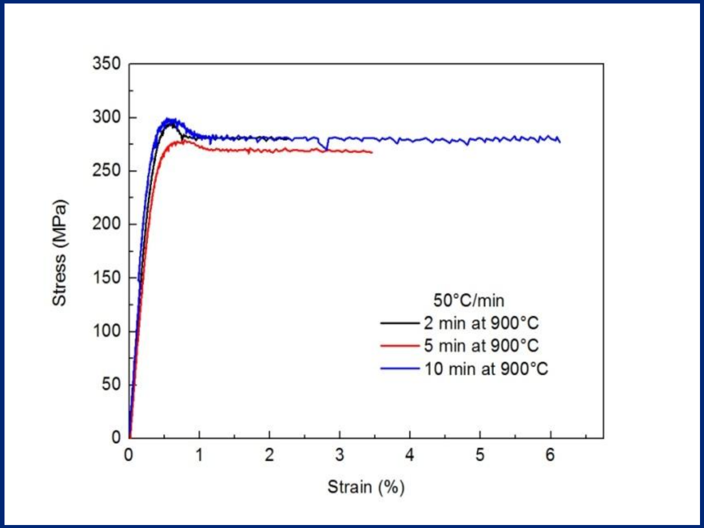


- Bimodal distribution of grain size with ultrafine and micrometric grains
- Coarsened grains are defect free and very clean
- In the ultrafine areas the grain size is well above 100 nm

Tensile Properties

50°C/min

Holding time (min)	Relative density (%)	Yield Stress (MPa)	UTS (MPa)	Elongation at fracture (%)
2	96,7	289	296	2,3
5	95,6	271	279	3,2
10	98,3	294	300	5,7



Absence of plastic instability

Tensile Properties

100°C/min

Holding time (min)	Relative density (%)	Yield Stress (MPa)	UTS (MPa)	Elongation at fracture (%)
2	97,2	336	347	2,0
5	95,8	286	291	0,8
10	96,8	289	298	2,8

150°C/min

Holding time (min)	Relative density (%)	Yield Stress (MPa)	UTS (MPa)	Elongation at fracture (%)
2	96,6	279	284	1,8
5	94,4	279	287	2,5
10	94,6	266	270	0,9

Conclusions
Thermal stability and sintering behaviour

1. In the as cryomilled powder the resisting stress applied by dislocations is much higher that the driving stress;
2. The Zener stress due to oxide particles is negligible;
3. Nanostructure and dislocation density enhance sintering whereas high resistance to plastic deformation retards deformation.
4. large density of dislocations may activate a dislocation pipe diffusion mechanism,
5. since about 1% of atoms belong to dislocations in the cryomilled powder.

International conference presentations

✓L'Initiation aux Logiciels d'Analyse des Materiaux par Diraction des Rayons X et des Electrons", 16 - 18 April 2013, Faculte de Physique, USTHB, Algiers, Algeria.

✓ EuroPM2012, 16 - 19 September 2012, Basel, Switzerland.

✓Third African School and Workshop on X-Rays in Materials, Some Established Techniques and Practical Applications, UCAD, Senegal, January, 23 - 28, 2012.

✓Euromat, 12 - 15 September 2011, Montpellier, France

✓Second African School and Workshop on X-Rays in Materials, Some Established Techniques and Practical Applications, Cheikh Anta Diop University of Dakar, Senegal, January, 19 - 24, 2009.

Some recent scientific productions…

✓S.Diouf , A. Molinari, Materials Letters 111 (2013) 17-19

✓S. Diouf et al., Powder Metallurgy 56 (5) (2013) 420-426

✓S. Diouf et al., Powder Metallurgy 55 (3) (2012) 228 – 234

✓S. Diouf, A Molinari, Powder Technology 221 (2012) 220-227

✓A. Molinari,et al. Int. J. Powder Metall., 2012, vol. 48, no. 6, pp. 31-39

Acknowlegments

✓ University of Trento

✓ Prof. Alberto Molinari (PhD adviser)

✓ ASP 2014 organizers

Thank you…

Thermal Stability of The Cryomilled Copper
Energy Stored By Dislocations And Grain Boundary

$$\Delta H_{edge} = \rho_{edge} \frac{Gb^2}{4\pi(1-\nu)} \ln\left(\frac{R_e}{r_0}\right)$$

$$\Delta H_{screw} = \rho_{screw} \frac{Gb^2}{4\pi} \ln\left(\frac{R_e}{r_0}\right)$$

$$\Delta H_{gb} = 3.3 \frac{\gamma_{gb}}{D}$$

	ΔH_{screw}	ΔH_{edge}	ΔH_{disl}	ΔH_{gb}	ΔH_{total}
As-milled	**5,99**	**9,42**	**7,70**	**6,33**	**14,03**
290°C	**1,44**	**2,26**	**1,85**	**4,89**	**6,74**
400°C	**0,74**	**1,17**	**0,96**	**4,30**	**5,26**
500°C	**0,40**	**0,63**	**0,52**	**3,16**	**3,68**
600°C	**0,45**	**0,70**	**0,58**	**1,96**	**2,54**