EFFECT OF SILVER IMPURITIES ON THE MECHANICAL BEHAVIOR OF COPPER NANOWIRES: AN ATOMISTIC SIMULATION

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www.gnm.cl

Copper 2013, Santiago, Dec. 2nd. 2013

Grupo de NanoMateriales, www.gnm.cl

Universidad de Chile

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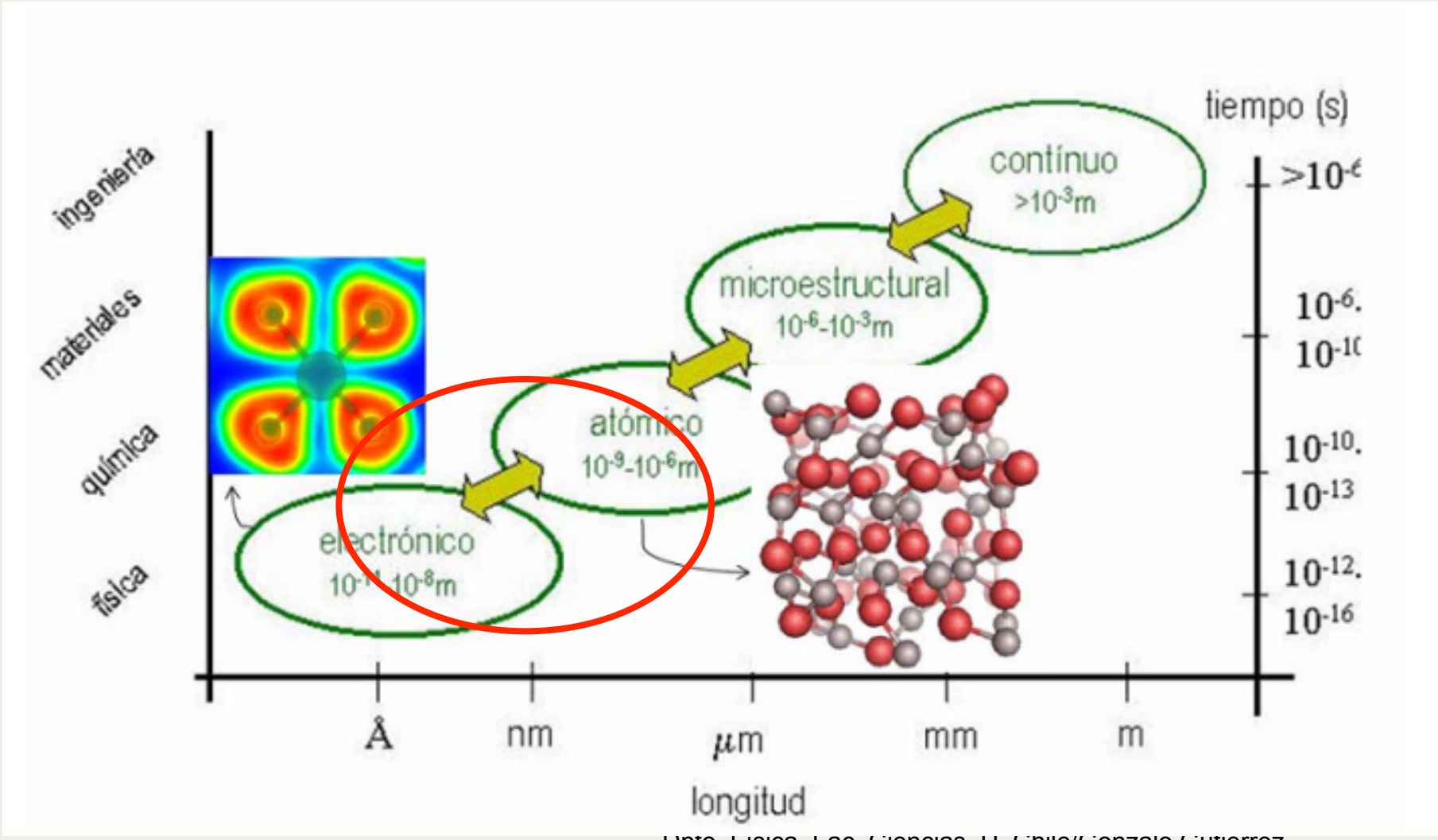
- Postgraduate students: F. González, Y. Navarrete, N . Amigo
- Undergraduate pregrado por año
- Colaboradores en Chile y el extranjero.

Atomic level simulation



Outline

- Motivation: qualification of copper products
- Effects of impurities in copper
- Silver impurities in nanowires
    - mono-crystal
    - poli-crystal
- Conclusions

Context

Codelco

Anodes
99.5%

Cathodes
99.99%

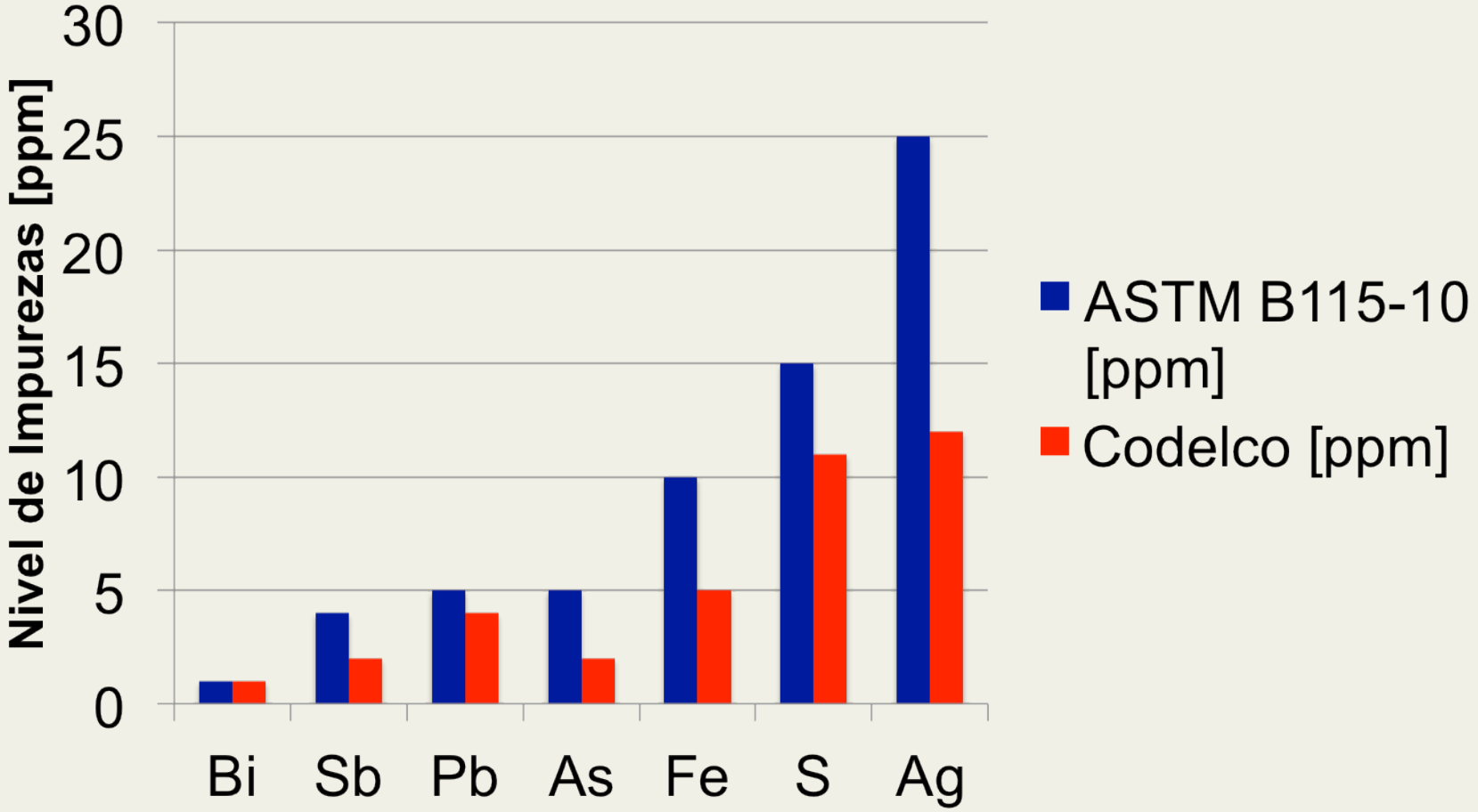
wires

Chemical analysis
Visual qualification

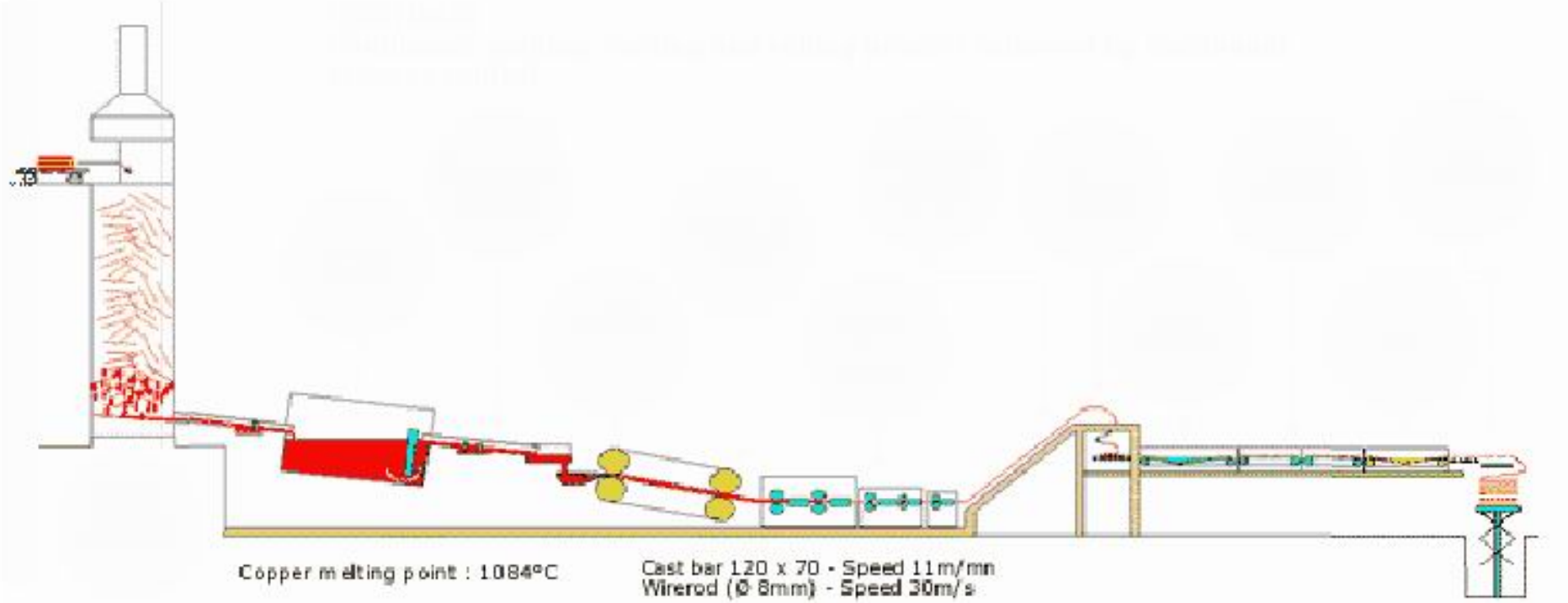
Chemical analysis
Mechanical test

(taken from Jil & Moya)

Chemical qualification: Cathode Grade A standard



From cathodes to wires



…qualification of the Cathodes (from Chile) is done form mechanical test performed on wire...(abroad)

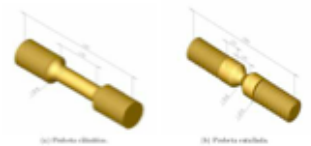
Determinación de Propiedades Mecánicas de Productos de Cobre

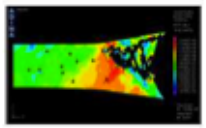
CODELCO
Orgullo de Todos

Proyecto CODELCO-IM2 36-11
Responsable de Proyecto: M.Ignat

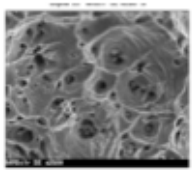
Marzo 2012

- Miguel Ignat: Análisis propiedades mecánicas
  - Docteur Ingenieur (1977), Docteur en-Sciences (1983)

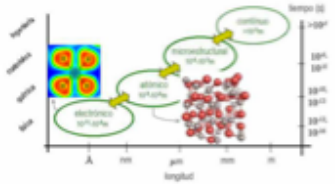


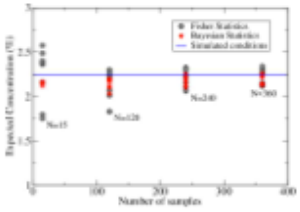


- Álvaro Valencia: Análisis Termodinámico
  - Dr-Ing. Ruhr-Universität Bochum, Alemania, 1993.

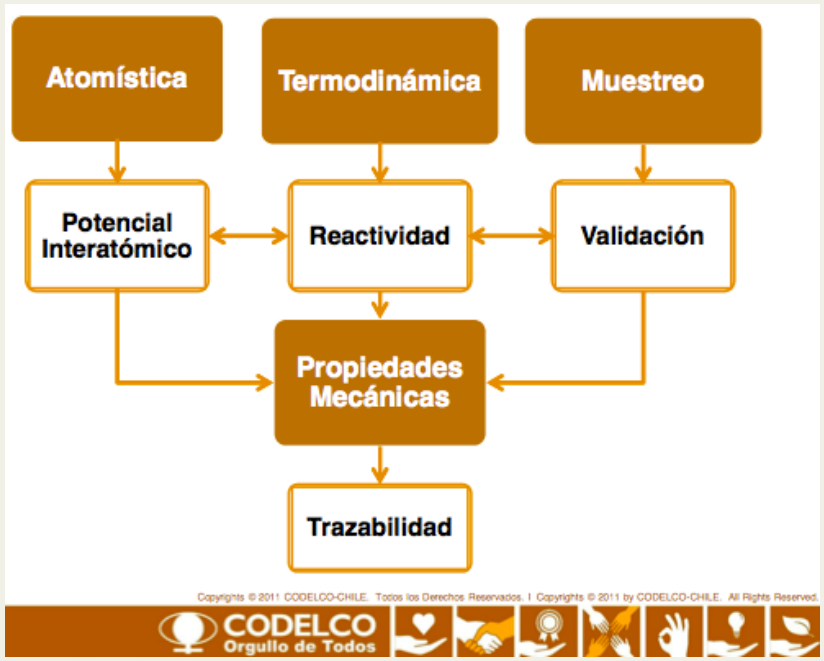


- Gonzalo Gutiérrez: Modelización Atómica
  - Doctor en Ciencias con Mención en Física, P. Universidad Católica de Chile, 1997





- Sergio Davis: Estadística de Muestreo
  - Ph.D in Applied Material Physics, Royal Institute of Technology (KTH), Estocolmo, Suecia (Septiembre 2009)

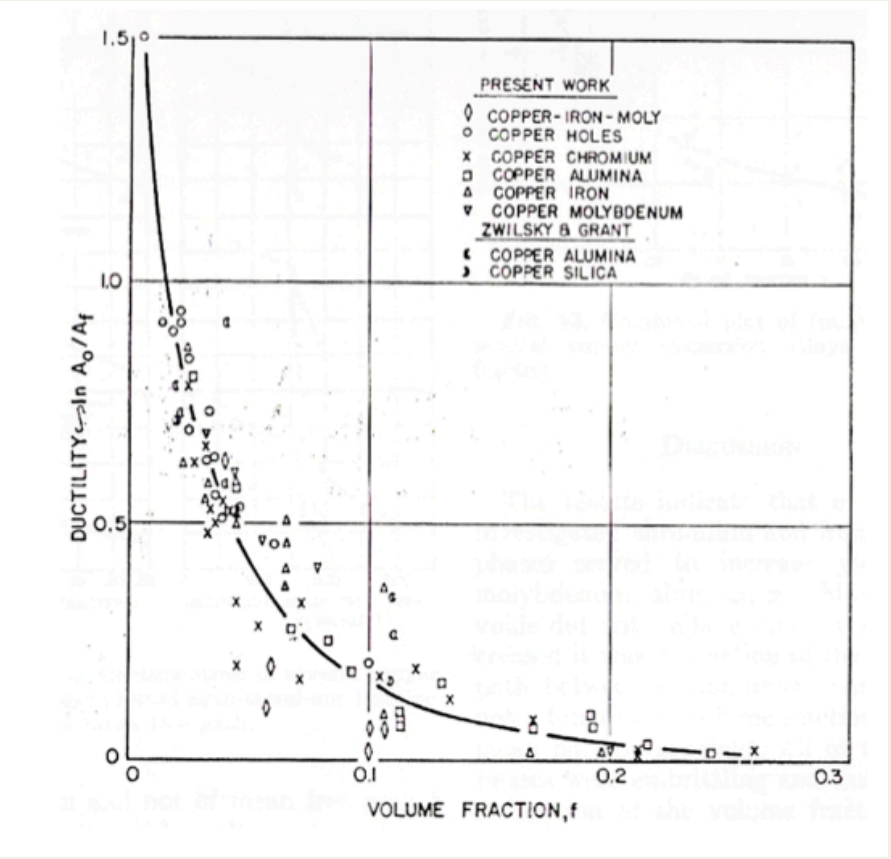


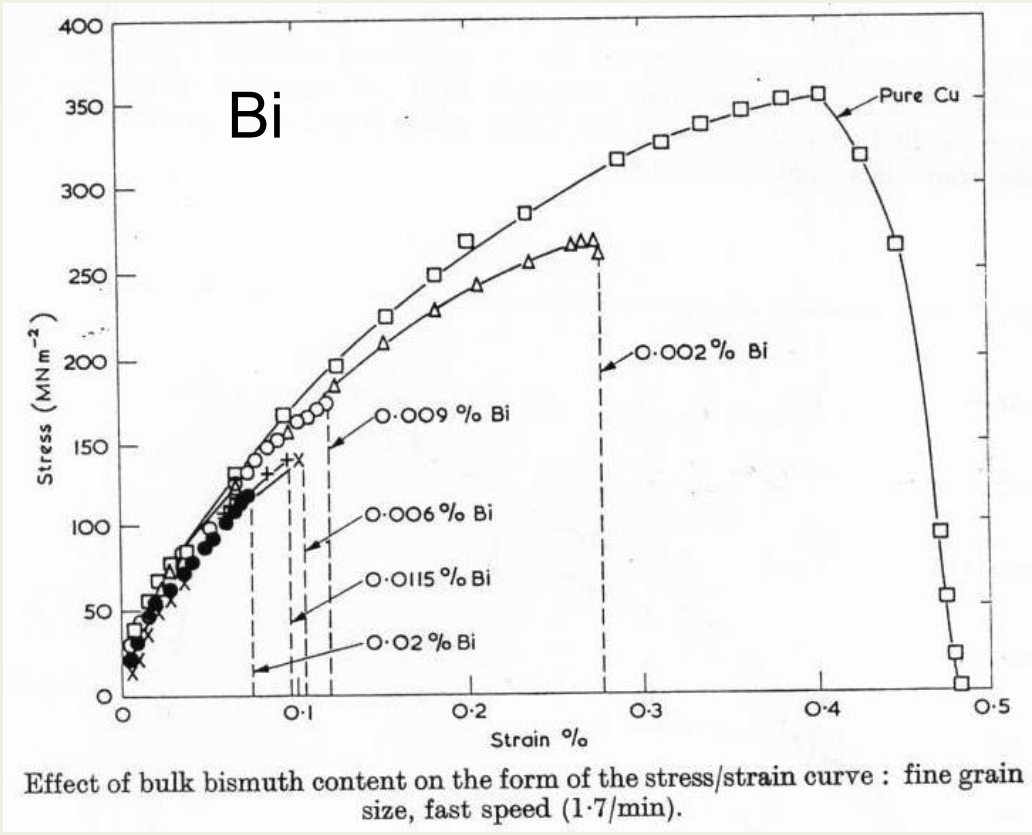
Goals

- To study the chemical and mechanical properties from anode-cathode-wire: complete traceability.
- To determine the effect of impurities on the mechanical properties ant the recristalization process
- To demonstrate the microestructural, chemical and mechanical discontinuity between cathodes and wires

To propose a mechanical qualification protocol for chilean copper products

Ductility of copper in terms of precipitates and impurities





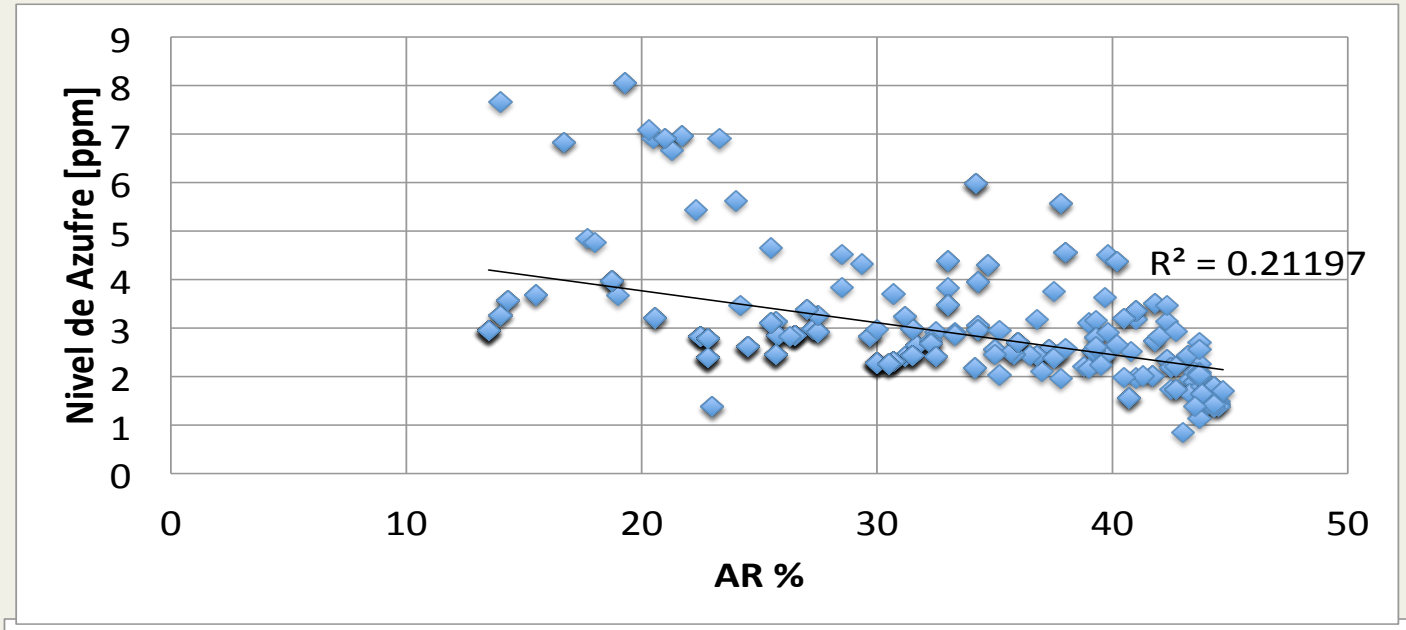
Effect of bulk bismuth content on the form of the stress/strain curve : fine grain size, fast speed (1·7/min).

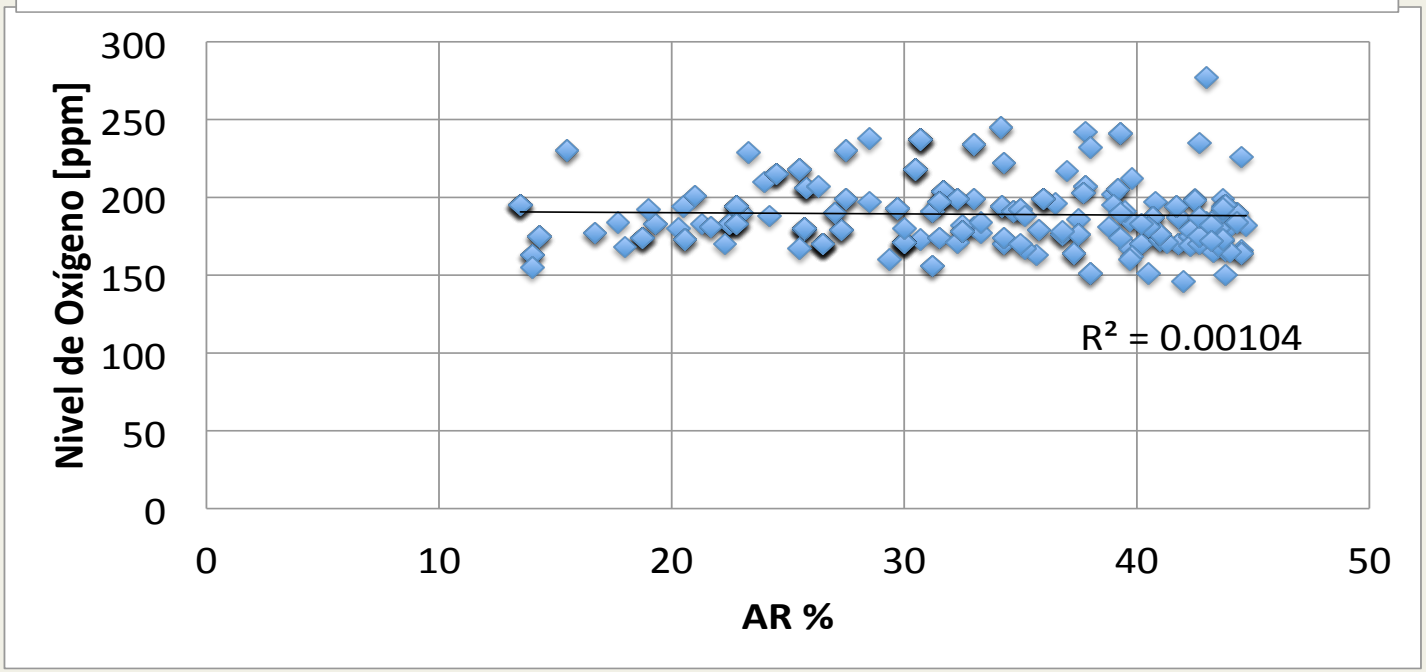
Hondros and McLean
Phil Mag 1974

W. M. Baldwin, B.I. Edelson – The effect of second phases on the mechanical properties of alloys. –
Transactions, American Society for Metals 55:230 – 250, 1962.

Cu become brittle with Bi

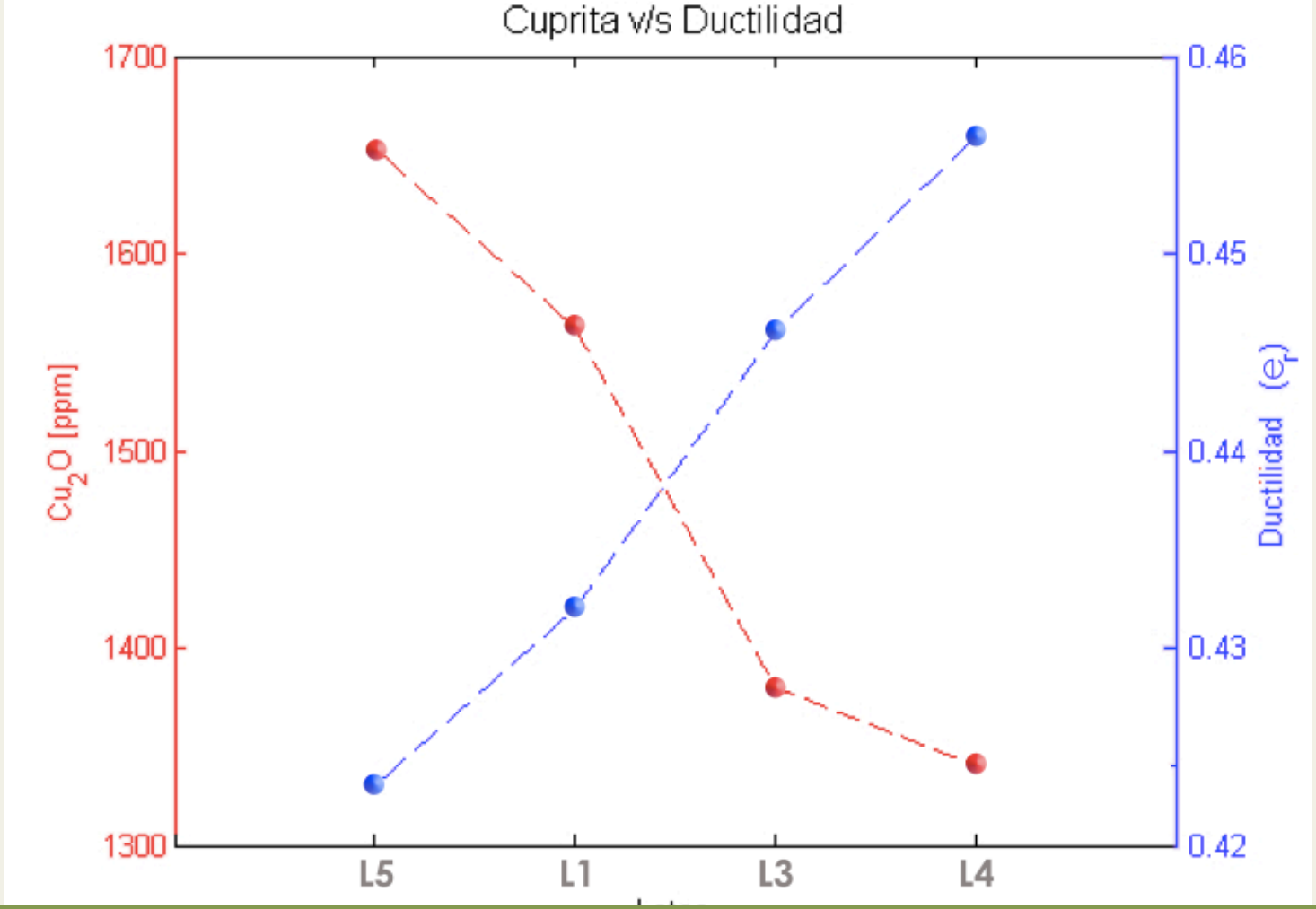
AR versus Nivel de Impurezas





*Fuente: Base de datos confidencial.

Previous work



*Fuente: R. González, P. Hidalgo - Estudio de propiedades mecánicas de cátodos y alambrones de cobre – U. de Chile 2006.

Can theory and simulation contribute to solve the problem? YES, we can!

Bismuth-induced embrittlement of copper grain boundaries

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[2]North Carolina State University, Materials Science & Engineering Department, Raleigh, North Carolina 27692, USA
[3]Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, D-70569 Stuttgart, Germany
*e-mail: chisholmmf@ornl.gov

"We find that the copper atoms that surround the segregated bismuth in the grain boundary become embrittled by taking on a more zinc- like electronic structure".

Nature Materials, Sep.2004

Bismuth embrittlement of copper is an atomic size effect

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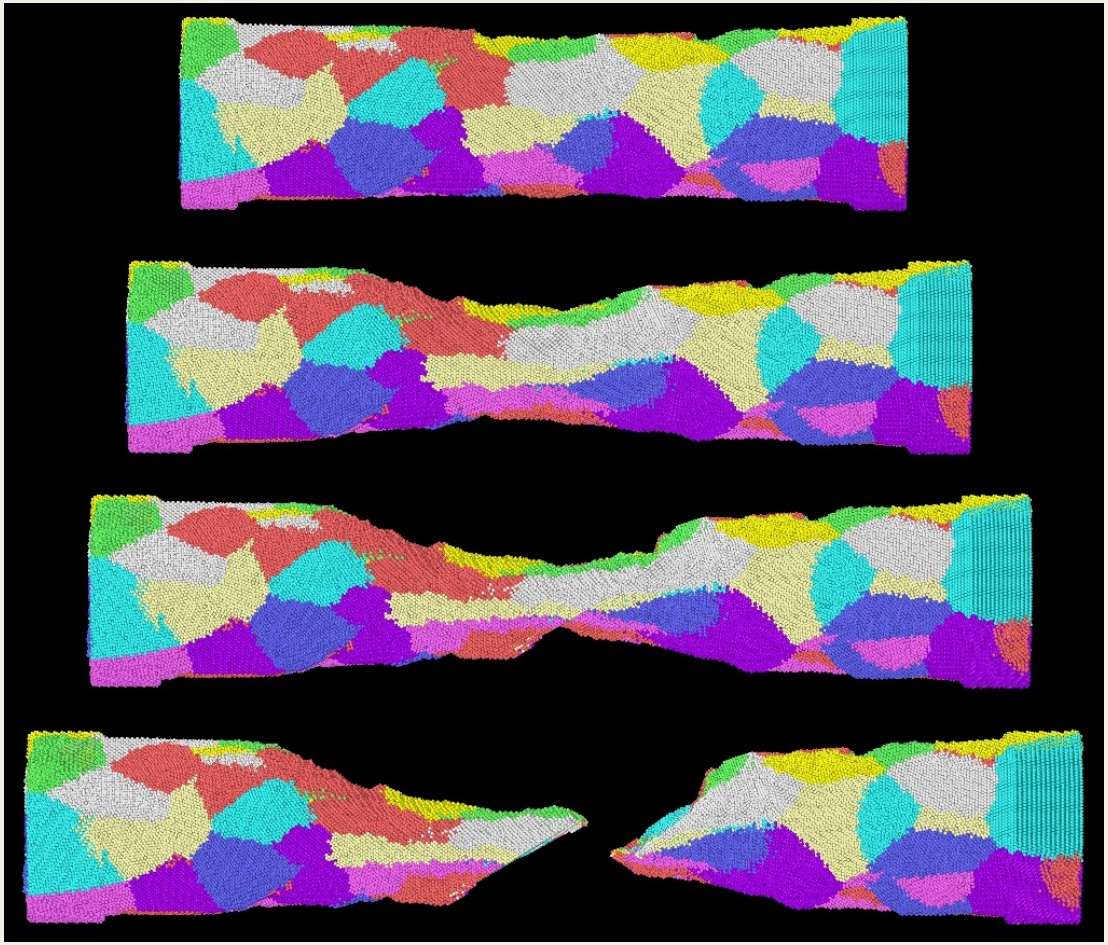
Embrittlement by the segregation of impurity elements to grain boundaries is one of a small number of phenomena that can lead to metallurgical failure by fast fracture[1]. Here we settle a question that has been debated for over a hundred years[2]: how can minute traces of bismuth in copper cause this ductile metal to fail in a brittle manner? Three hypotheses for Bi embrittlement of Cu exist: two assign an electronic effect to either a strengthening[3] or weakening[4] of bonds, the third postulates a simple atomic size effect[5]. Here we report first principles quantum mechanical calculations that allow us to reject the electronic hypotheses, while supporting a size effect. We show that upon segregation to the grain boundary, the large Bi atoms weaken the interatomic bonding by pushing apart the Cu atoms at the interface. The resolution of the mechanism underlying grain boundary weakening should be relevant for all cases of embrittlement by oversize impurities.

As A. H. Cottrell has put it "when a large force is applied to a crystal two things may happen: the atoms in the crystal may slide past one another; and they may pull apart." In the former case, a metal will fail gracefully with absorption of energy by dislocation generation and plastic deformation: the metal is said to be tough. Otherwise (in the latter case) the metal will fail by fracture. The applied force to cause failure is governed by the energy release rate, G, which is the energy that may be derived from the crystal plus loading train per unit area of crack advance[6]. In defining G one

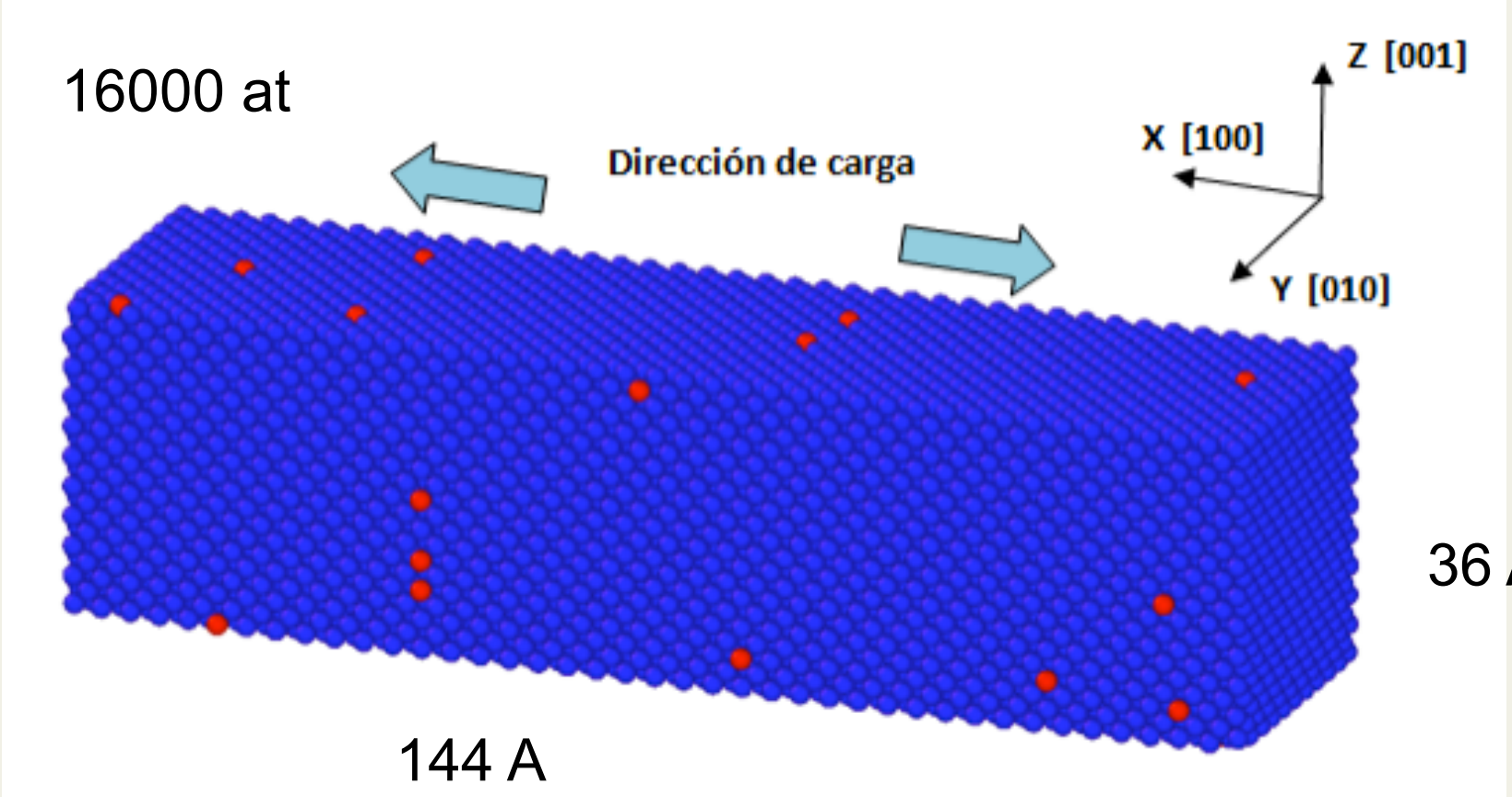
Dpto.

Mechanical properties by computer simulation: tensile test



Monocrystal copper nanowires with silver impurities

with **Nicolás Amigo**



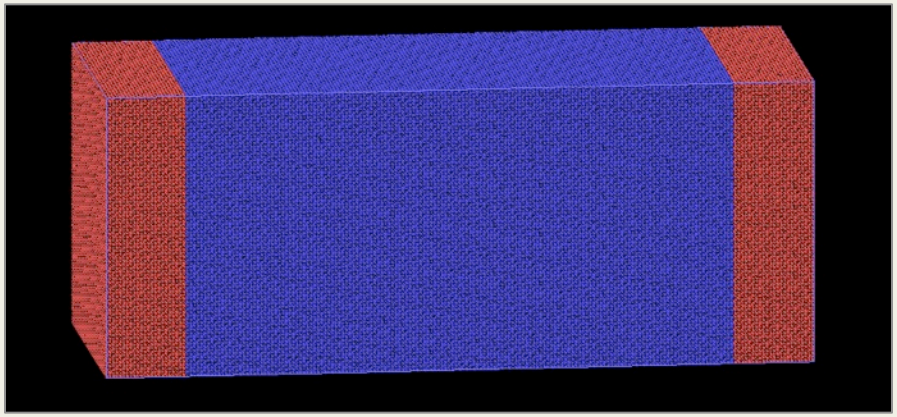
Technical details

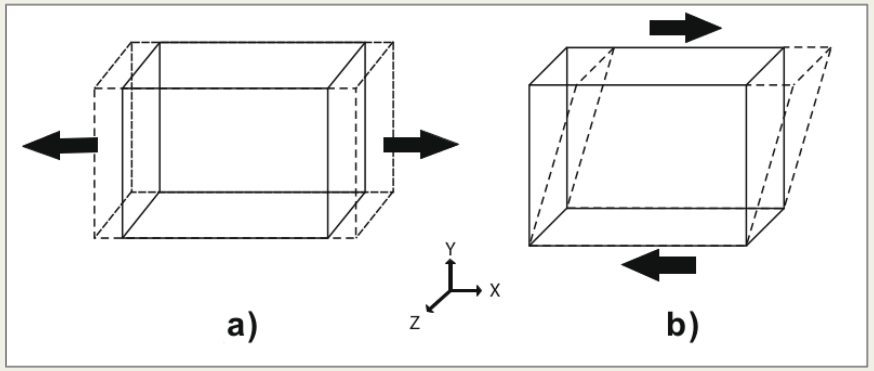
- Molecular dynamics simulation
- Embedded atom interatomic potential, Williams y Mishin (2006).
- T=0.1 K, NVT
- Deformation rate: 10^8 s^{-1}
- Surface impurities: 0.1% a 0.5%
- Approx 10 000 atoms

Testing the potential with the elastic constants

$$c_{ijkl} = \frac{\partial \sigma_{ij}}{\partial \varepsilon_{kl}}, \quad (i,j,k,l = x,y,z)$$

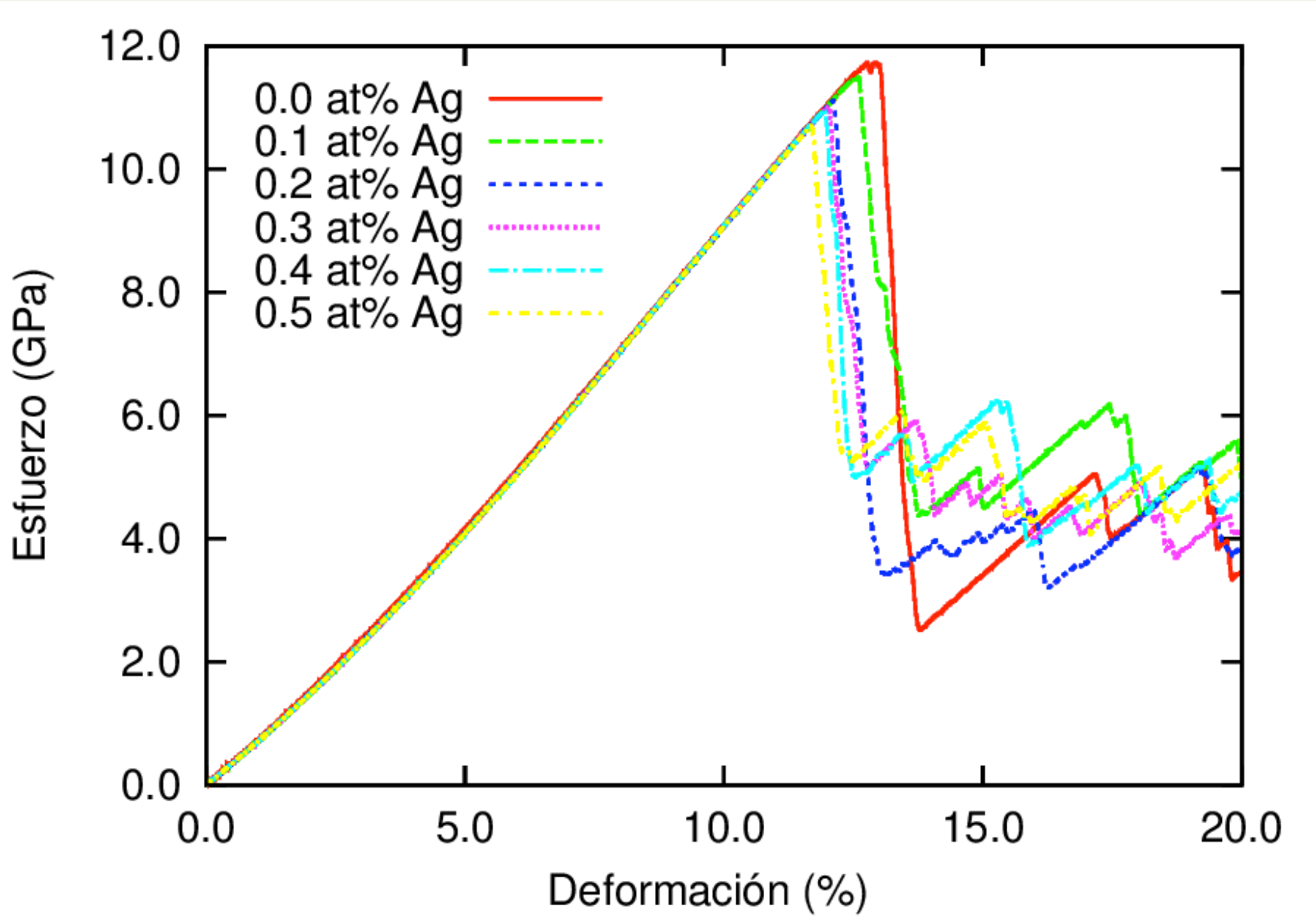
(Elastic properties of the bcc structure of Bismuth at high pressure,, G. Gutiérrez, E. Menéndez-Proupin, and A. K. Singh, Journal of Applied Physics 99, 103504 (2006))



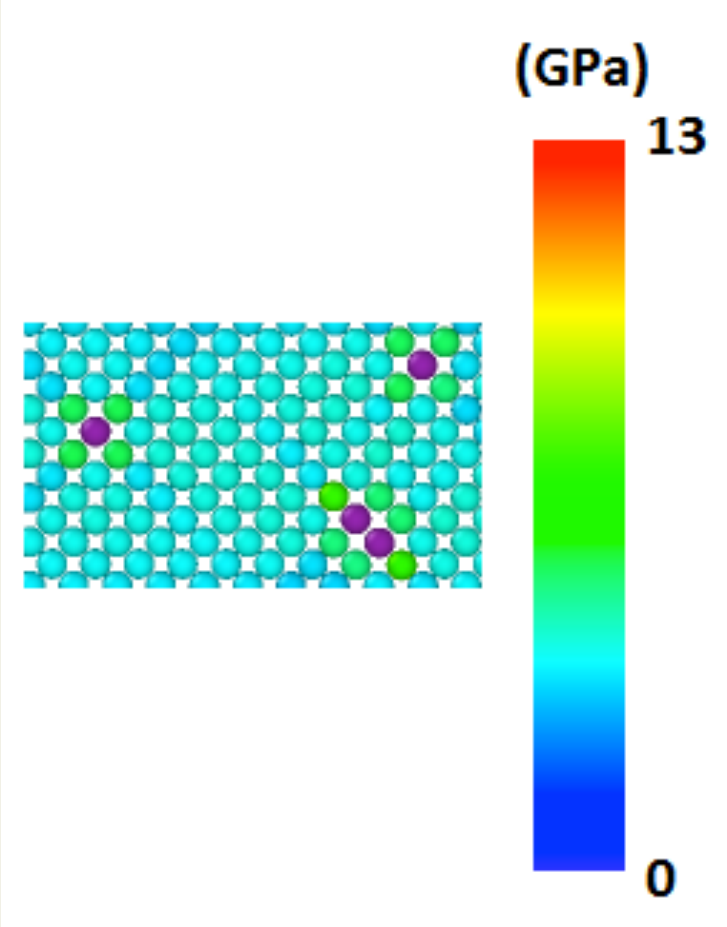


Constants	Literature [Gpa]	Simulation[Gpa]
C_{11}	176.2	171.0
C_{12}	125.0	126.3
C_{44}	82.0	79.9

Stress-strain curve



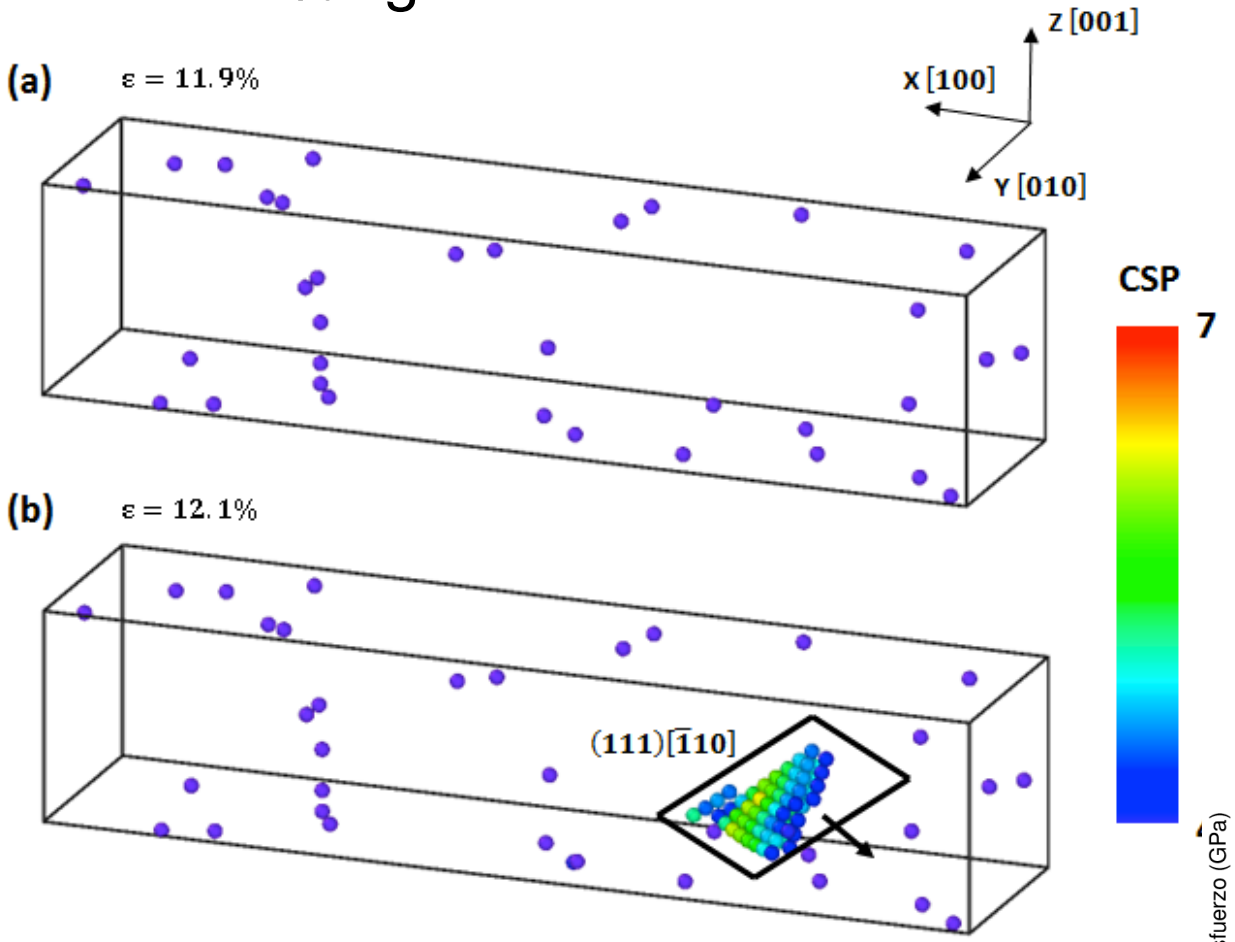
Dislocations begin at the surface

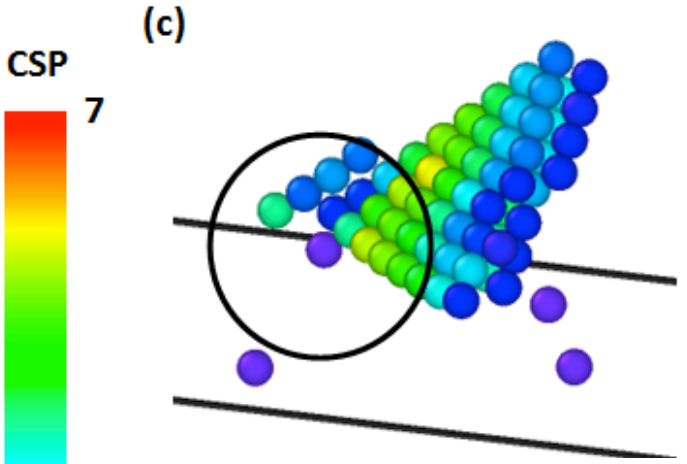


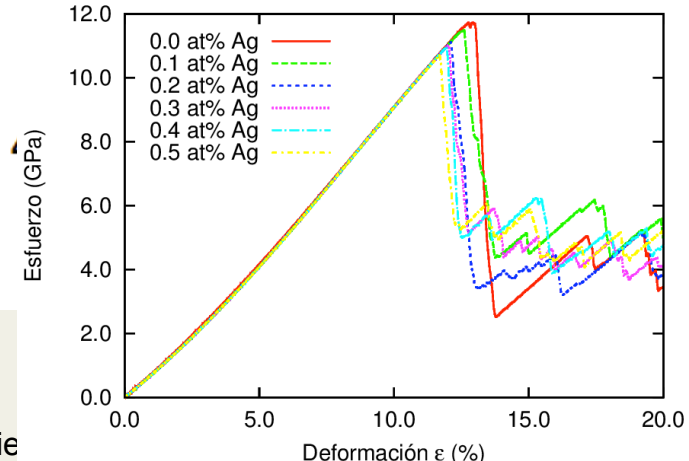
Surface stress because impurities

Emission of dislocations

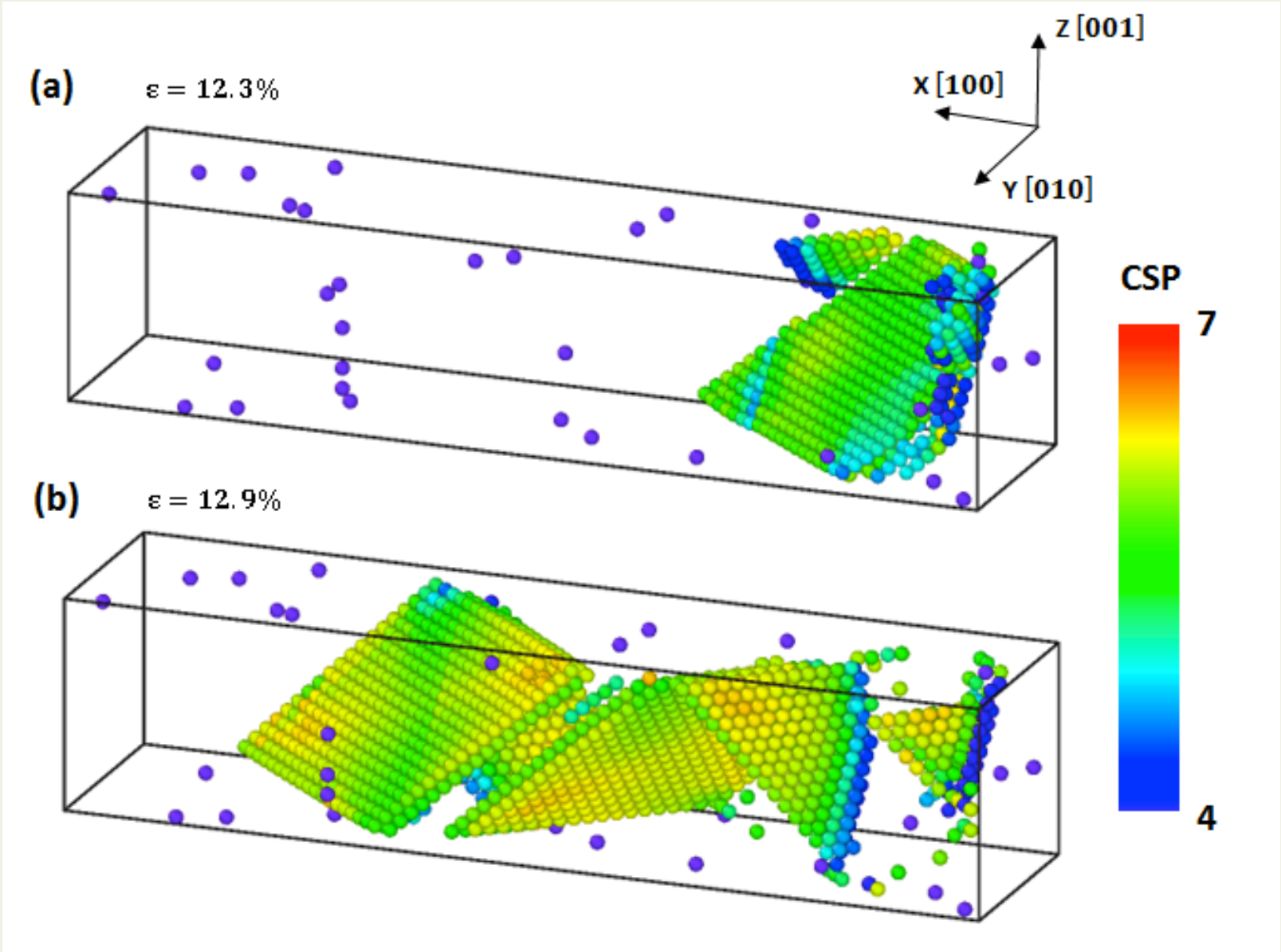
0.2 %Ag



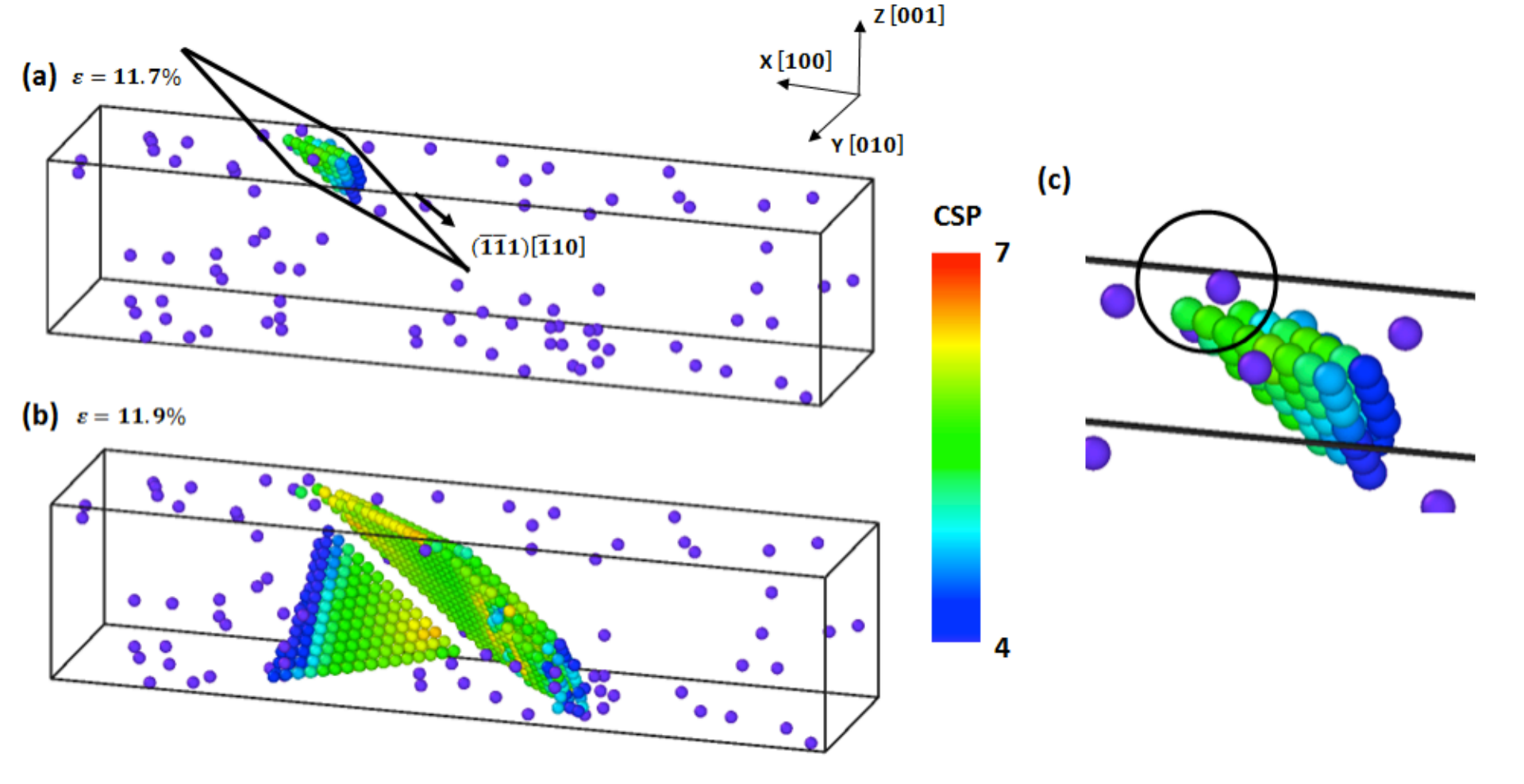




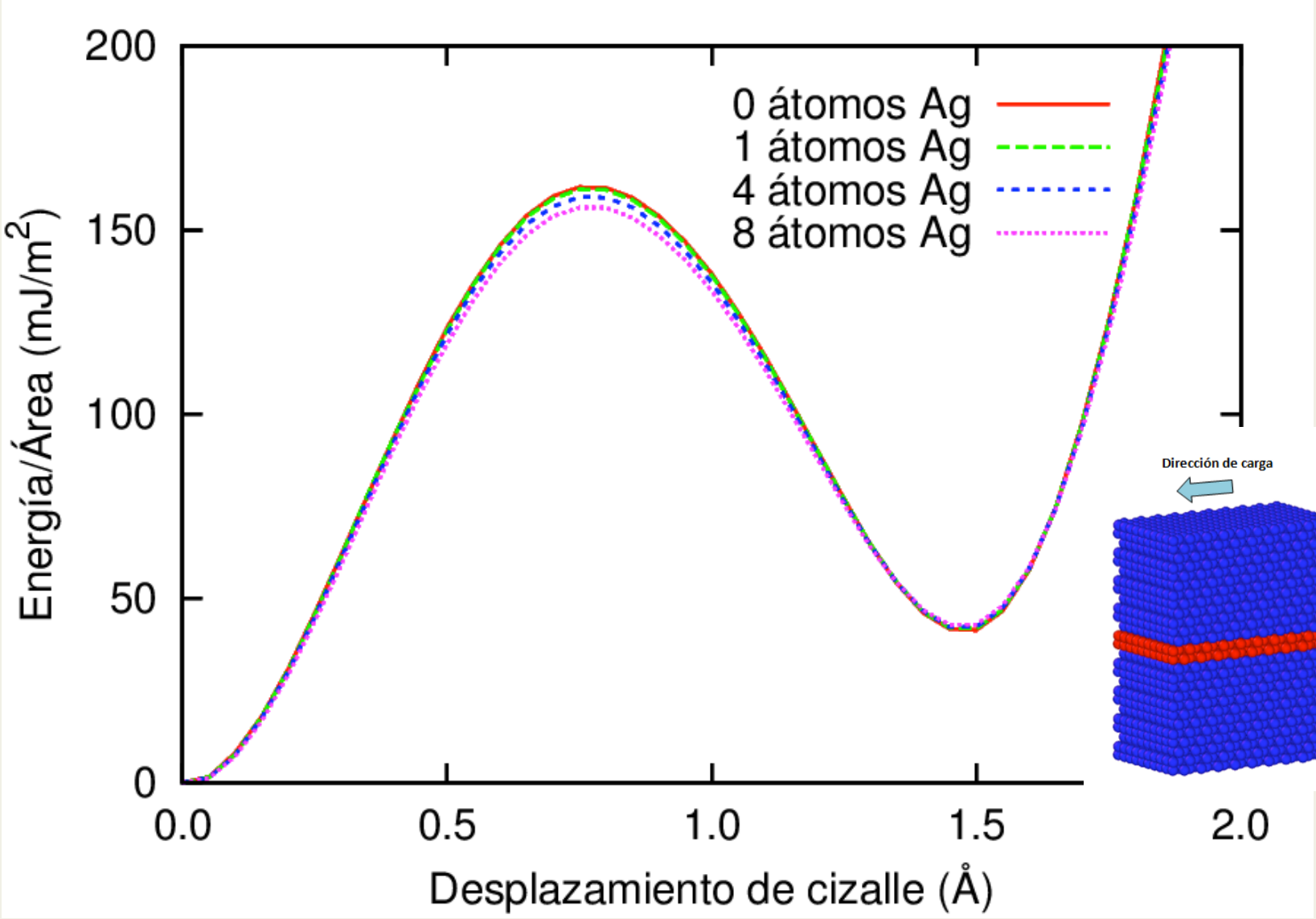
Next dislocation

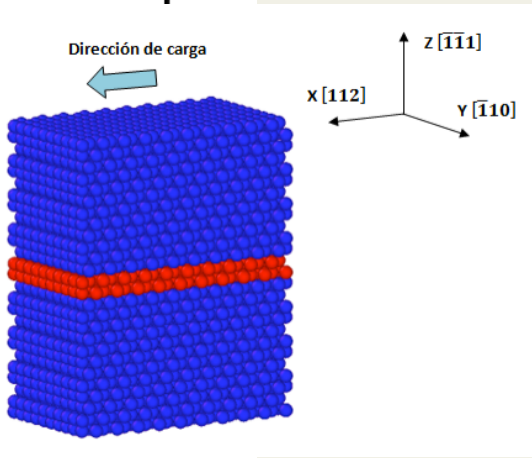


0.5%Ag case


(a) $\varepsilon = 11.7\%$
Z [001]
X [100]
Y [010]
$(\bar{1}\bar{1}1)[\bar{1}10]$
(b) $\varepsilon = 11.9\%$
CSP
7
4
(c)

Stacking fault energy





Unstable and stable staking fault energy in direction <112>

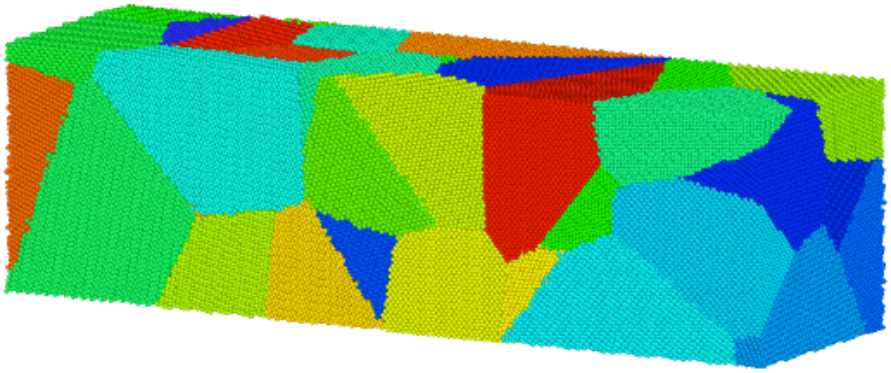
Contenido Ag (número de átomos)	γ_{usf} (mJ/m^2)	γ_{sf} (mJ/m^2)
0	161.7	41.4
1	161.2	41.8
4	159.0	42.2
8	156.2	42.8

Conclusions I

- Impurities:
  - no changes in the elastic regime
  - yield point decreases
  - promotion of dislocation emissions

Stacking faults energy calculations support this picture

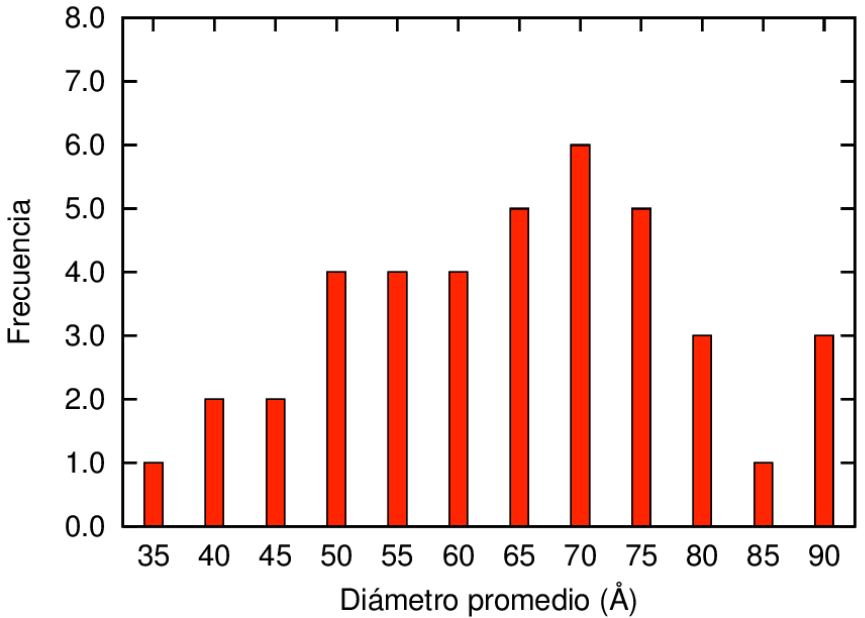
Impurities in poly-cristalline copper



126 A

430 A

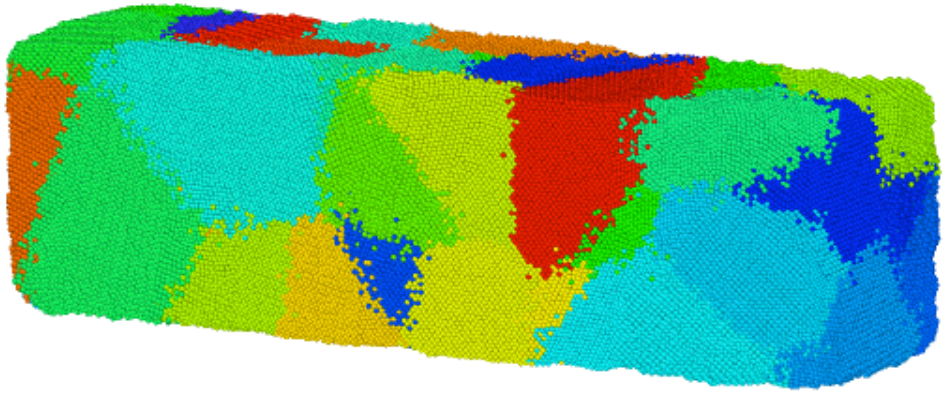
Diameter grains distribution



600 thousands atoms
40 grains

Dpto.

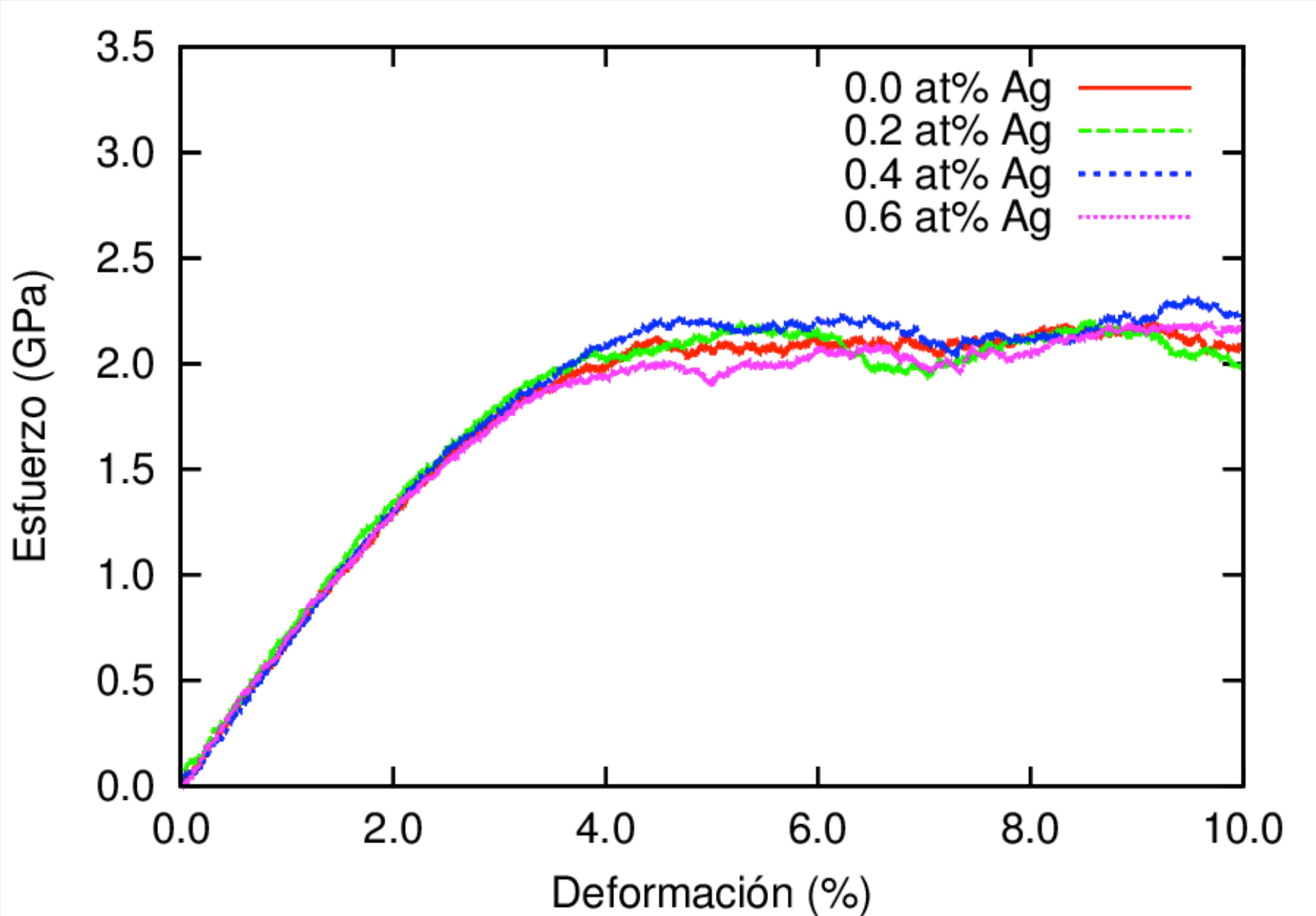
Technical details



-Ag: substitutional at Grains boundaries
-thermalization:
Langevin at 1000 K, 10 ps;
NVT 1000K, 100 ps;
Langevin at 300K, 10 ps;
NVT at 300 K 200 ps;
- During this process, several Stacking faults are generated.

Deformation rate: $5x10^{8}$ s^{-1}

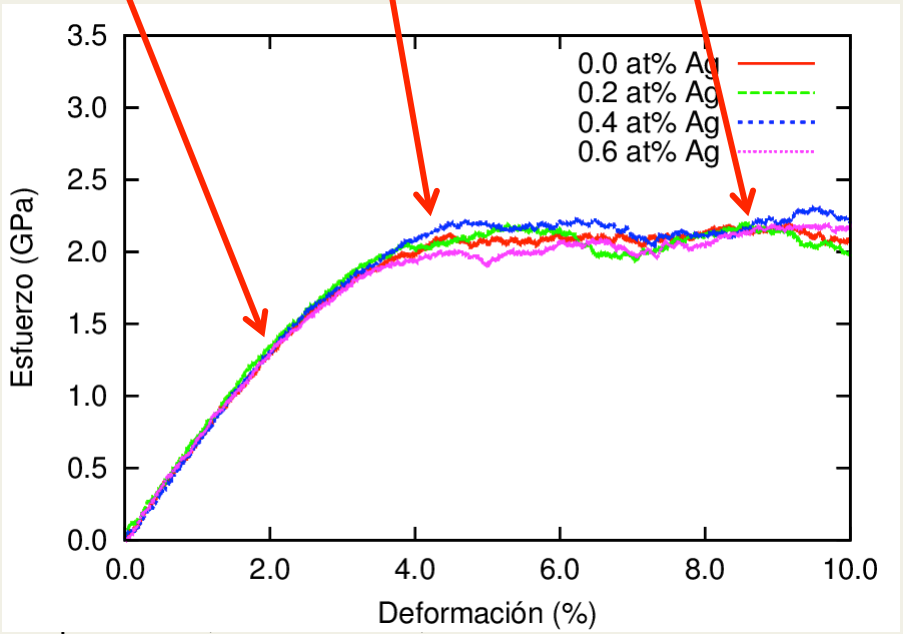
Stress-strain curve



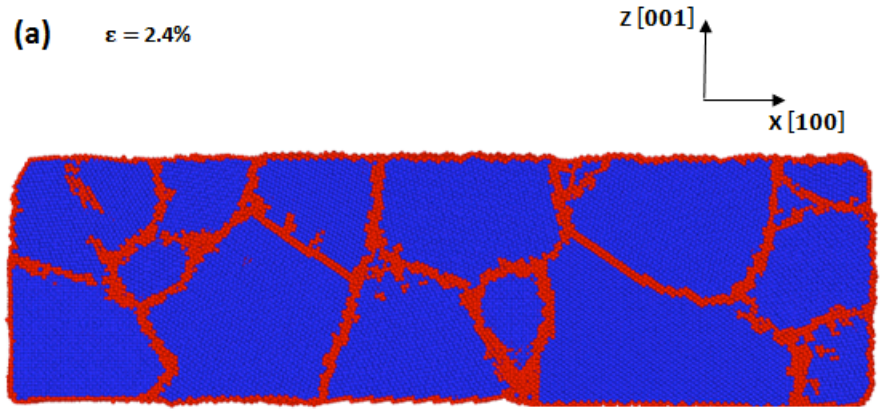
Young modules and other value

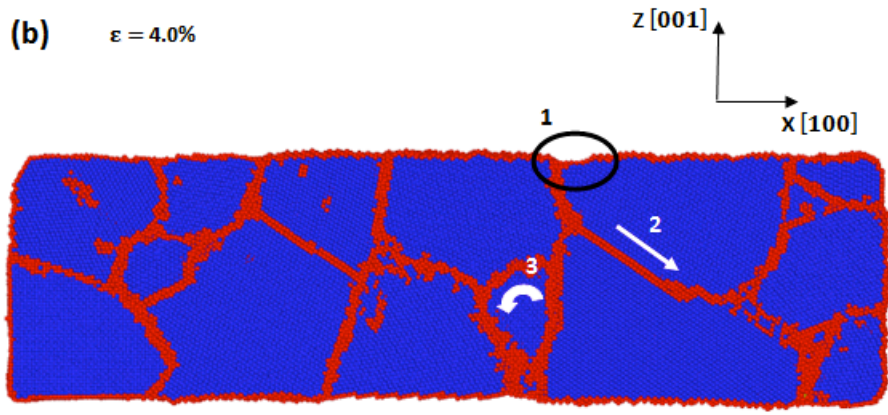
Sistema	E [GPa]	σ_f [GPa]	σ_{max} [GPa]	σ_p [GPa]
0.0 at % Ag	68.84	1.45	2.12	2.14
0.2 at % Ag	68.86	1.56	2.19	2.09
0.4 at % Ag	68.33	1.58	2.22	2.17
0.6 at % Ag	70.96	1.38	2.01	2.10

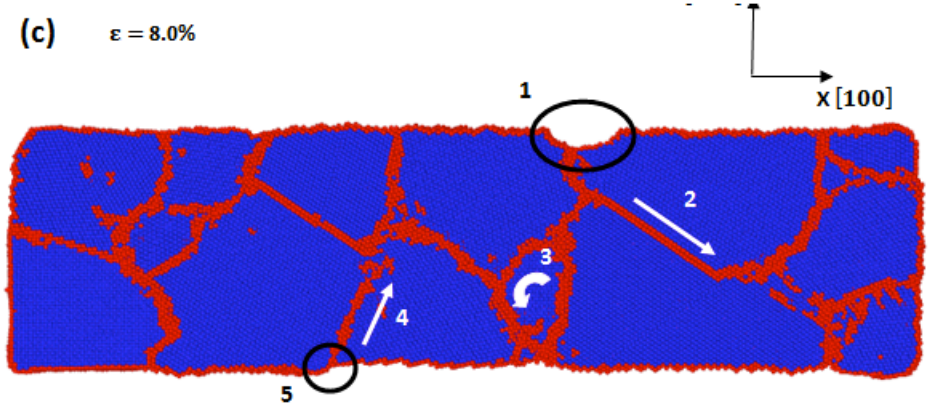
No significant changes!



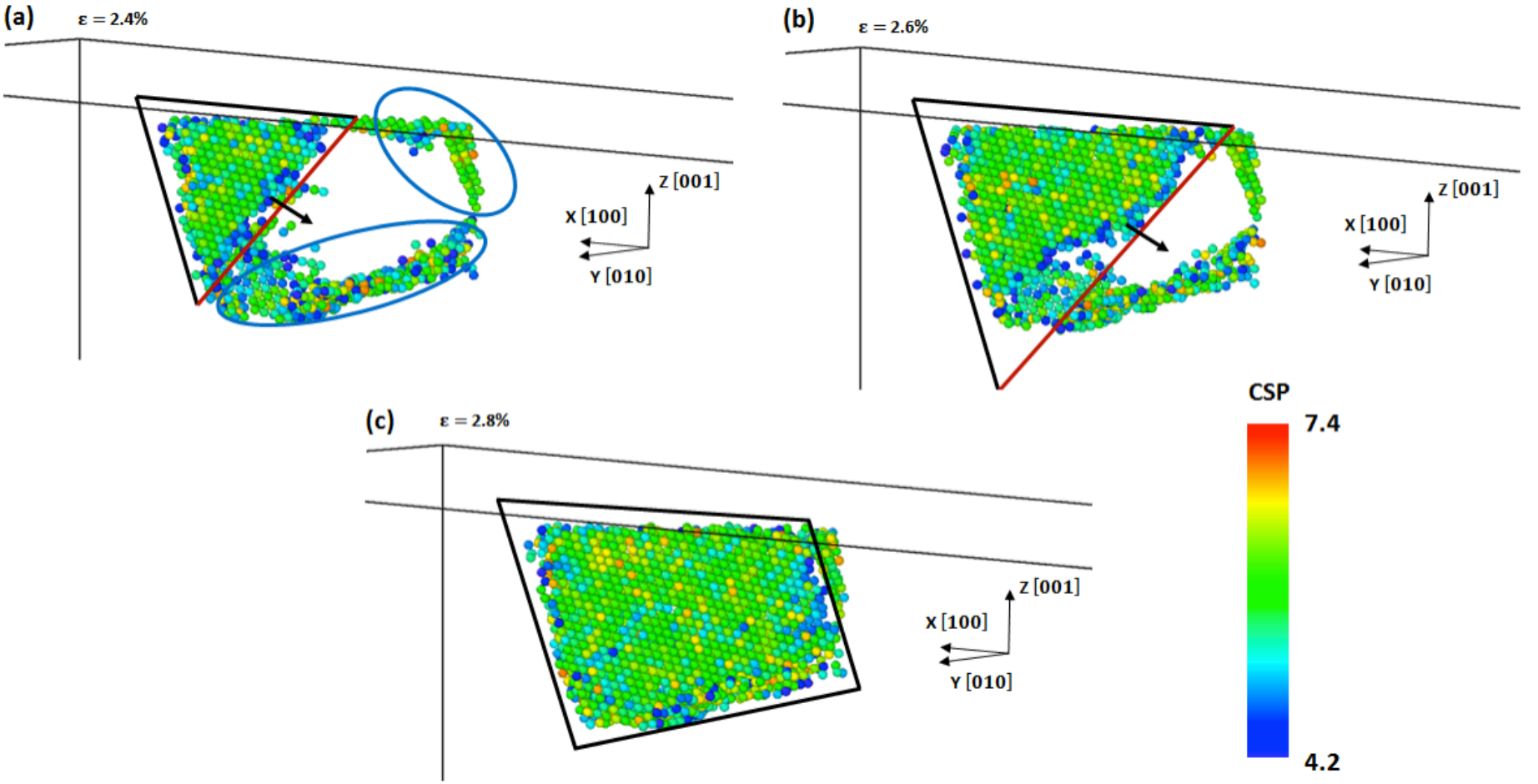
Mechanism of plasticity: rotation and sliding of grains



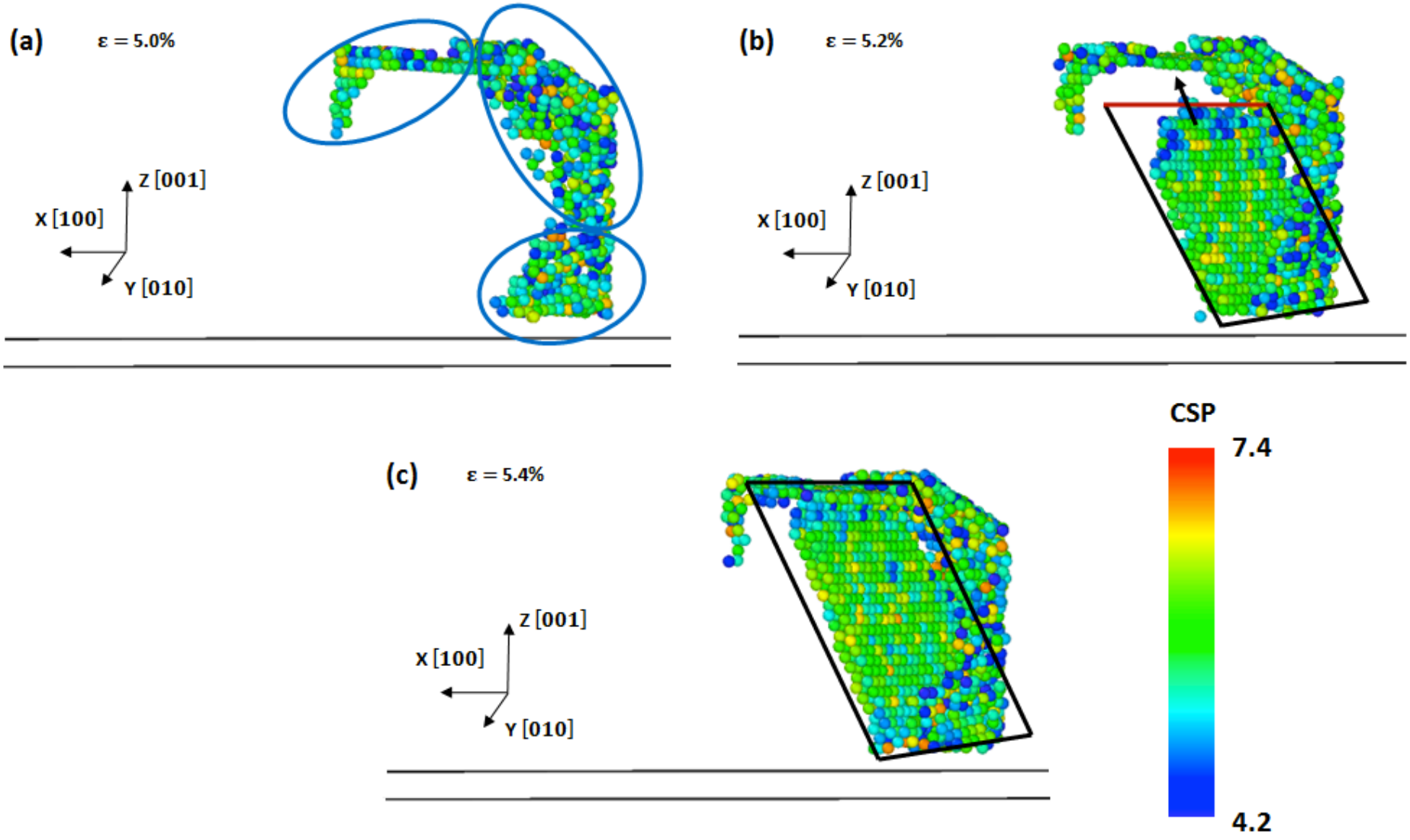


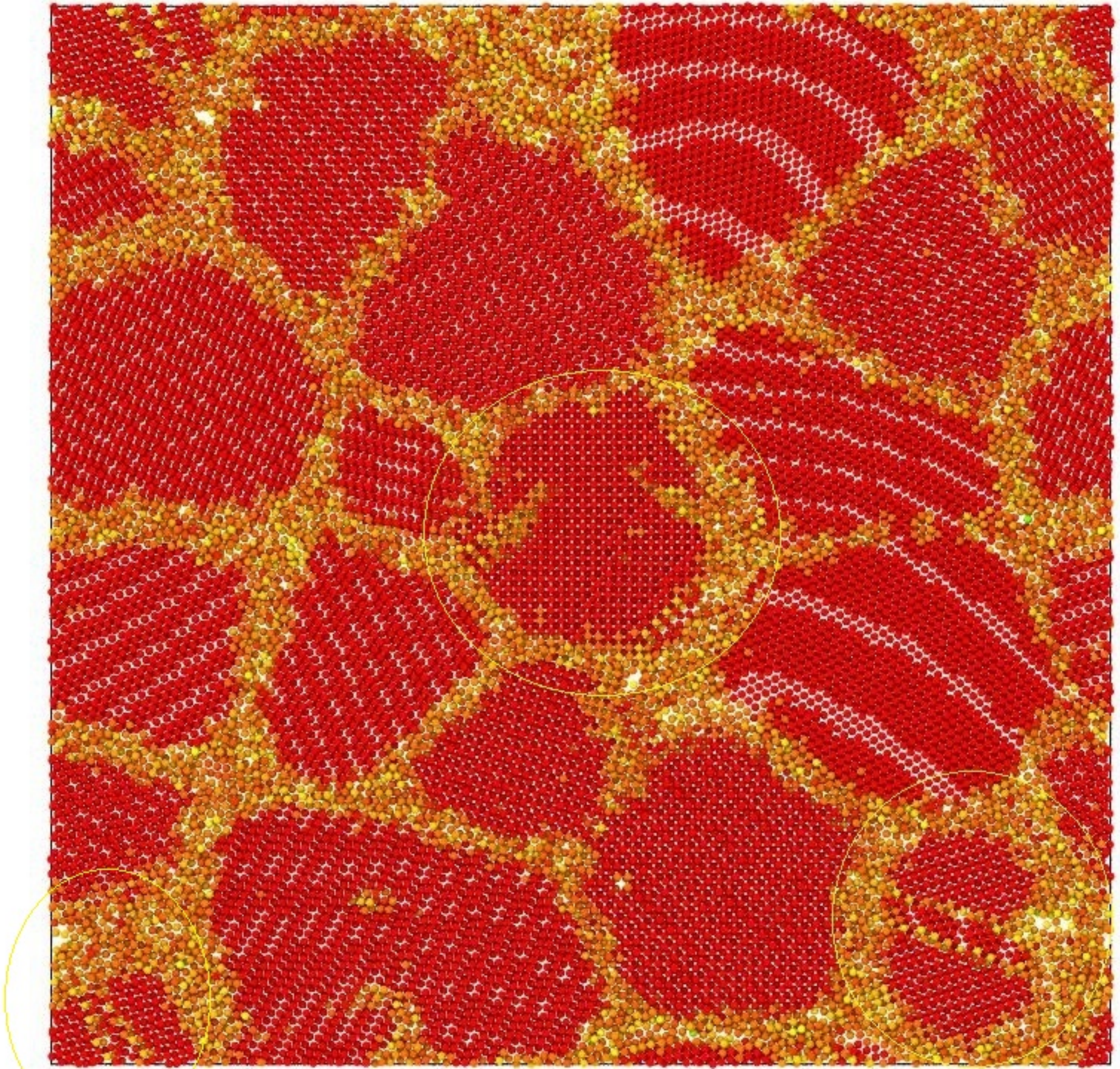


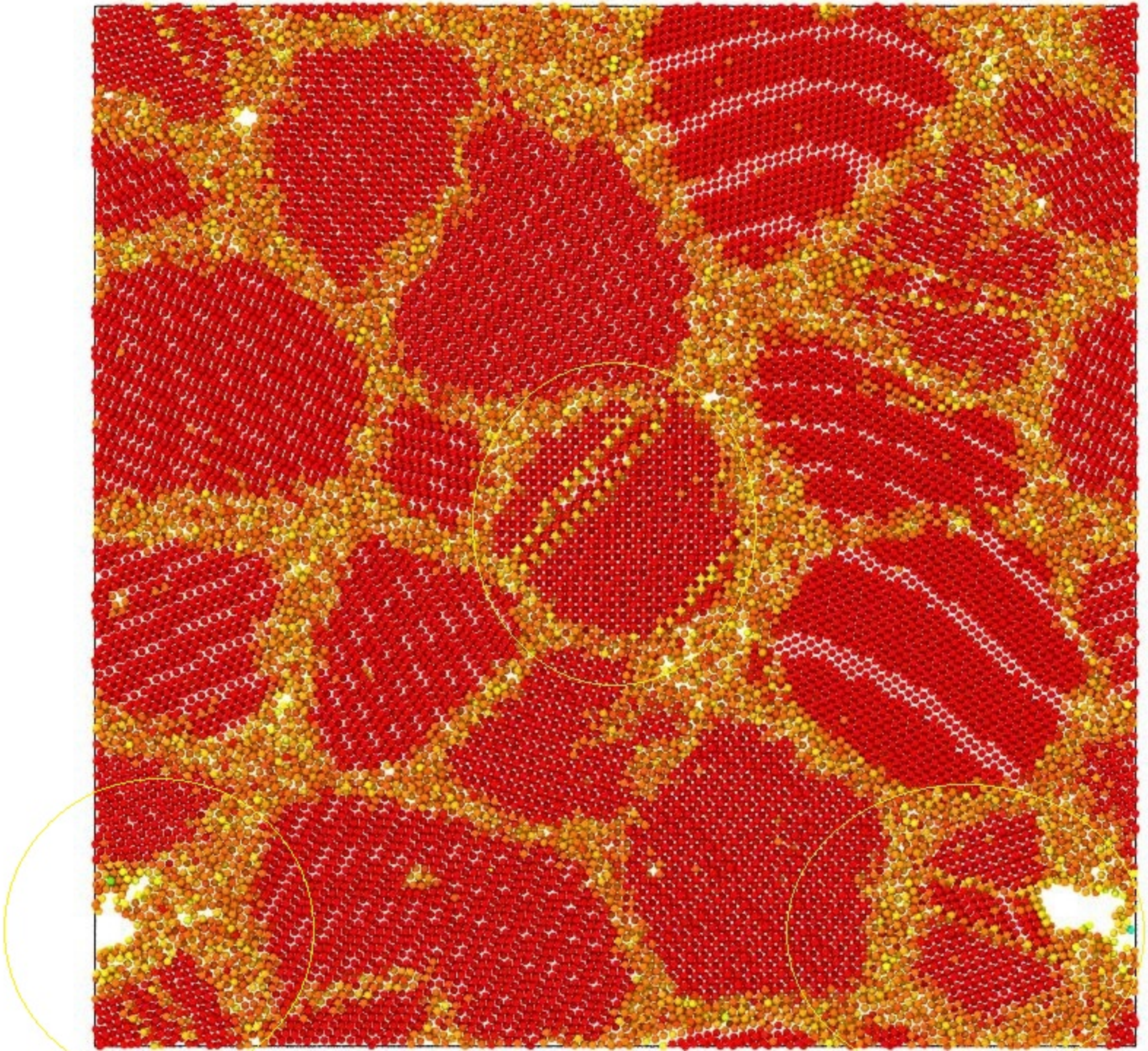
Dislocations at grains I



Dislocations at grains II







Conclusions II

- Impurities do not provoke significant changes for elastic nor plastic regime
- Plasticity is governed by grains rotation and sliding as well as by dislocations
- More study is needed to clarify the role of texture and grain size
- Nevertheless, is clear that there is no great changes in the mechanical properties, in good agreement with experiments.

¡Thank you!