International Spring School on Forefront Alloys and Advanced Materials for Extreme Conditions

15 – 17 May 2017

Sardinia, Italy

High-Energy Ball Milling: a powerful technique for the synthesis of new alloys and nanostructured materials

Sebastiano Garroni

UNIVERSIDAD DE BURGOS ICCRAM International Research Center in Critical RAw Materials for Advanced Industrial Technologies

Introduction

- Professor **Darwin Caldwell**

iCub

(RobotCub Consortium)

Introduction

- Q: Which challenges in the next Robot generation?

- A: «there are different aspects to be considered, the first one is, definitely, the <u>**material**</u>. The goal is to create soft robot which means flexible, adaptable, materials. Only in this manner the interaction with human will become «soft»….so we look the **materials**, then sensors, motors etc.»

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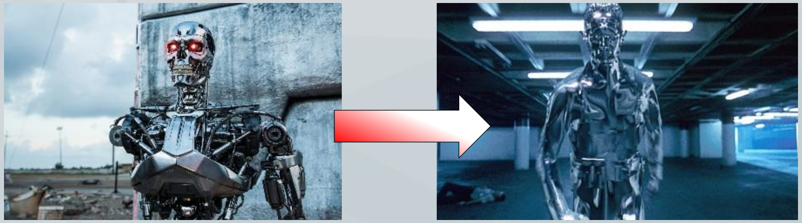
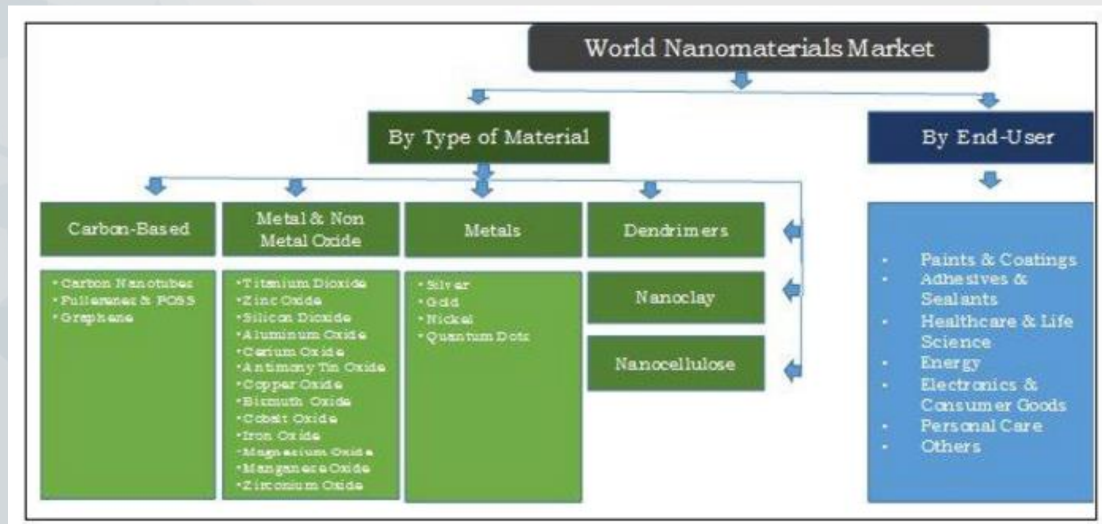


Nanomaterials Market[1]

- $15 million (2015)
- $55 million (2022)



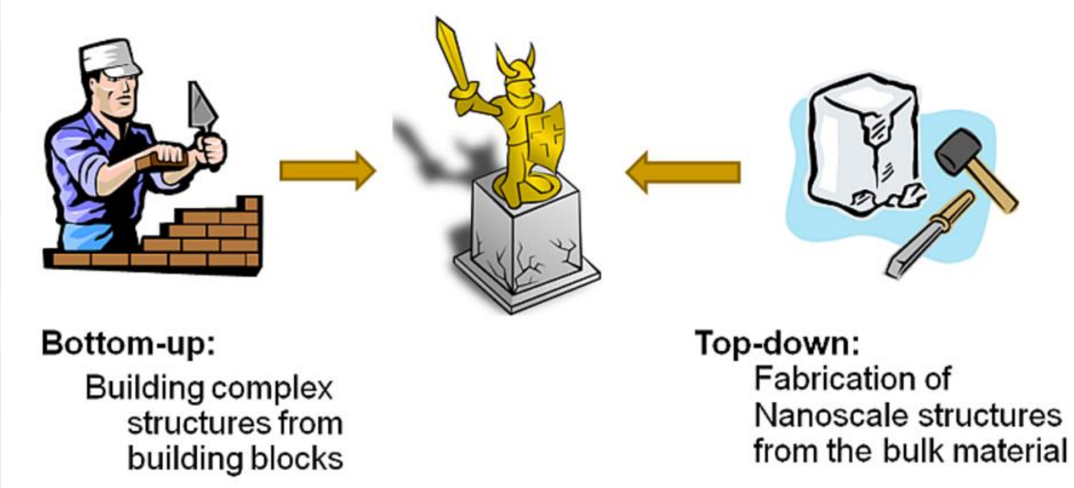
About Manufacturing?

[1] Allied Market Research Report 2015.

Manufacturing of Nanomaterials

Approaches[1]

- Bottom-up
- Top-down



[1] **Peter Rodgers, Nanofabrication: Top down, bottom up, Nature Nanotechnology, 2006**

Manufacturing of Nanomaterials

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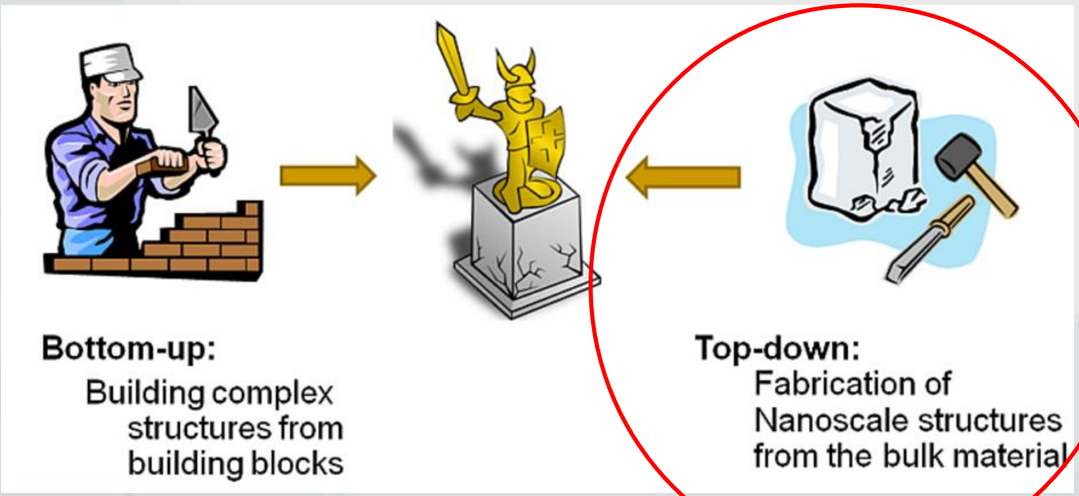


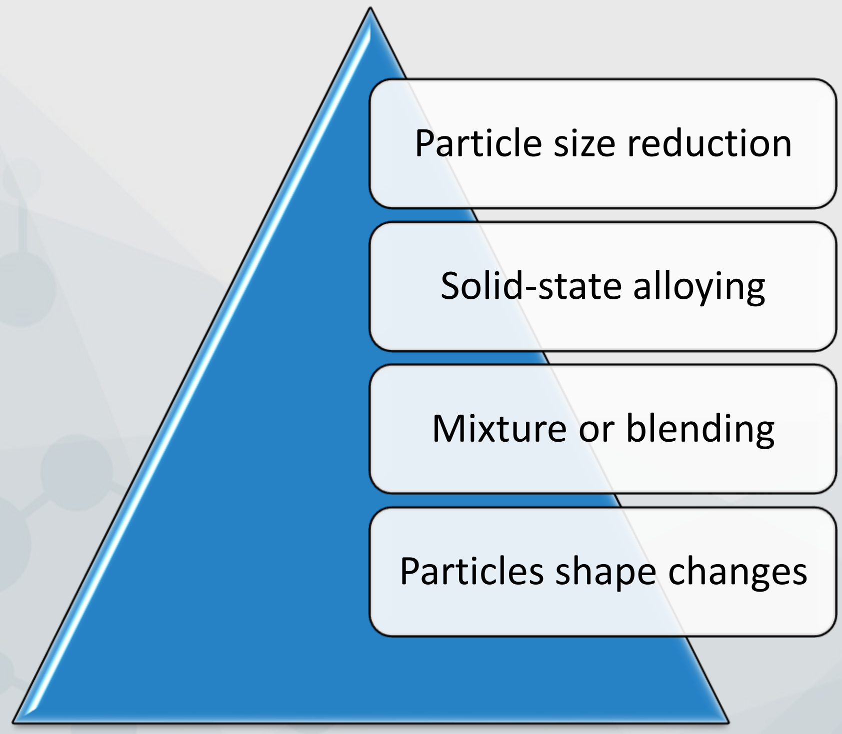
Mechanical Milling

[1] **Peter Rodgers, Nanofabrication: Top down, bottom up, Nature Nanotechnology, 2006**

Mechanical milling

Milling Applications

- Minerals Processing
- Ceramics Processing
- Powders Metallurgy



Main Objectives[1]

[1] **Hans J. Fecht, Nanostrucutred Materials and Composites prepared by solid state processing.**

Mechanical milling

Type of Mill devices[1]

- Tumblers mills
- Attrition mills
- Shaker mills
- Vibratory mills
- Planetary mils

<u>Choice of milling equipment</u>

[1] **C. Suryanarayana, Prog. Mater. Sci. 46 (2001) 1.**

Mechanical milling

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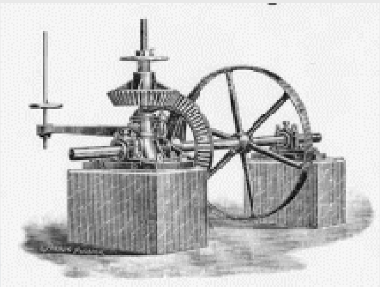
Wind mill



Flour Mill

4 kW coffee Mill

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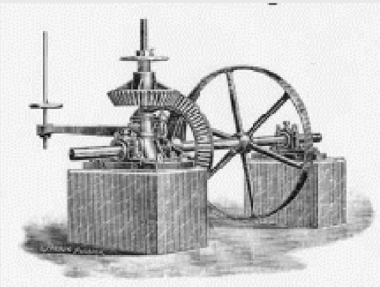

Flour Mill

4 kW coffee Mill

Industry

Horizontal mills

Laboratory

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[1] **TP Yadav, RM Yadav, DP Singh, Nanoscience and Nanotechnology 2012, 2: 22-48**

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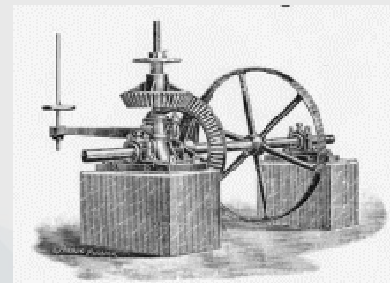

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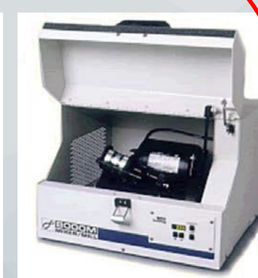

Shaker

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Ball milling

Research and technological impact

- 20.000 Publications (Scopus)
- 30.000 Patents (Orbit)

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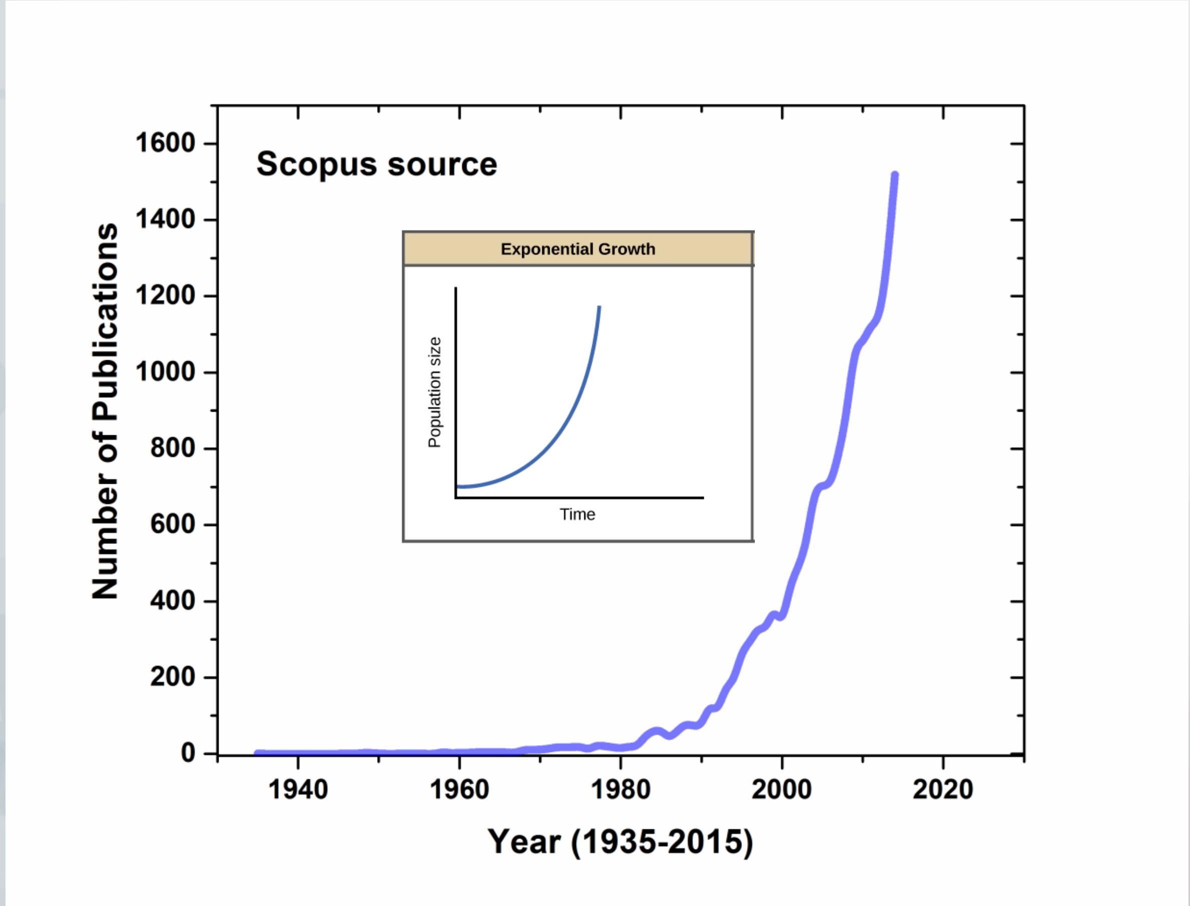
Ball milling: Historical development

- Exponential Growth



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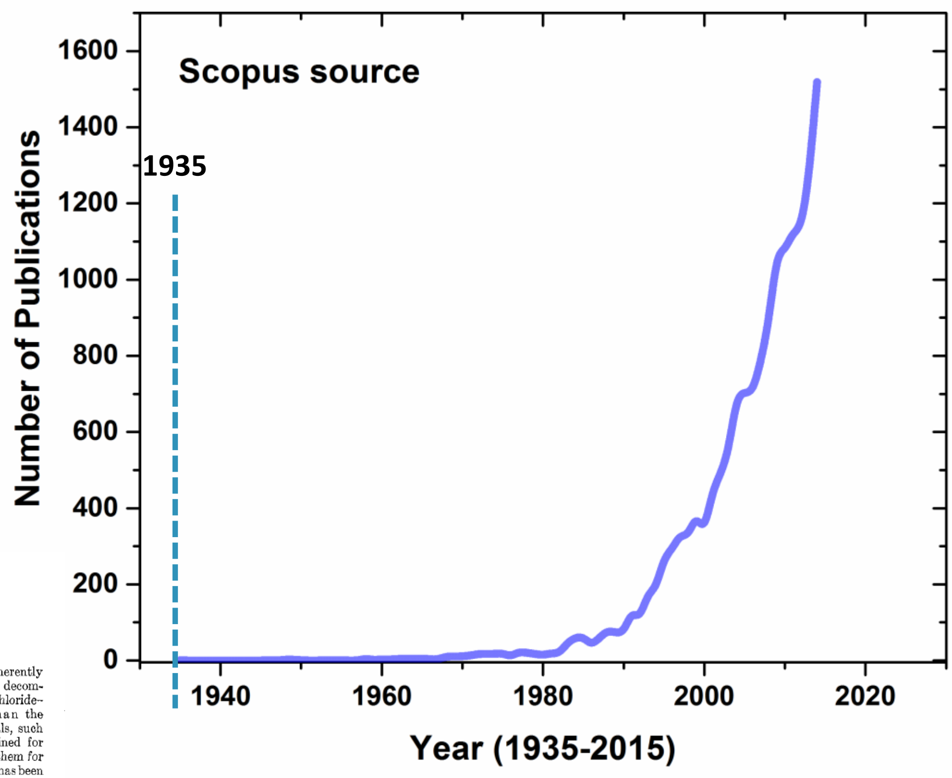

Notes on the J. Lawrence Smith Fusion

MARK O. LAMAR, WALLACE M. HAZEL, AND WM. J. O'LEARY
Norton Company, Research and Chemical Laboratories, Worcester, Mass.

As many prominent analysts continually fail to agree on the alkali content of rocks, minerals, refractory substances, and the like, and report different results on one and the same material after preliminary treatment by the J. Lawrence Smith method of fusion, it has been thought worth while to describe some of the experiences met in the Norton Company Research Laboratories with the J. Lawrence Smith treatment of difficultly attackable materials, in the hope that the results may lead to some improvement of the method as now standardized.

There have been pointed out several sources of possible disagreement between different analysts over the alkali content of the same material when using the standard J. Lawrence Smith fusion. Since different substances are not thereby decomposable to the same extent, it has been suggested that the samples first be ground to some standard size, that the fusions be made at a higher temperature than is now customary, that the calcium carbonate and ammonium chloride flux be mixed together by ball-milling, and that correction of the mixed chlorides for accompanying magnesium be appropriately emphasized. The suggested improvements have been applied in the analysis of so-called beta-alumina.

all these materials are inherently much more difficult to decompose with ammonium chloride-calcium carbonate than the highly siliceous materials, such as rocks, usually examined for alkalies. In analyzing them for sodium and potassium it has been found (1) that comparable disintegrations by the J. L. Smith method can be obtained only when the samples have been ground to a comparable, controlled size; (2) that highly aluminous samples low in silica must be ground so that all the sample passes 200-mesh, and that an "impalpable feel" is not a sufficient criterion to insure complete decomposition; (3) that the highest temperature of

Standardization of the alkali content method

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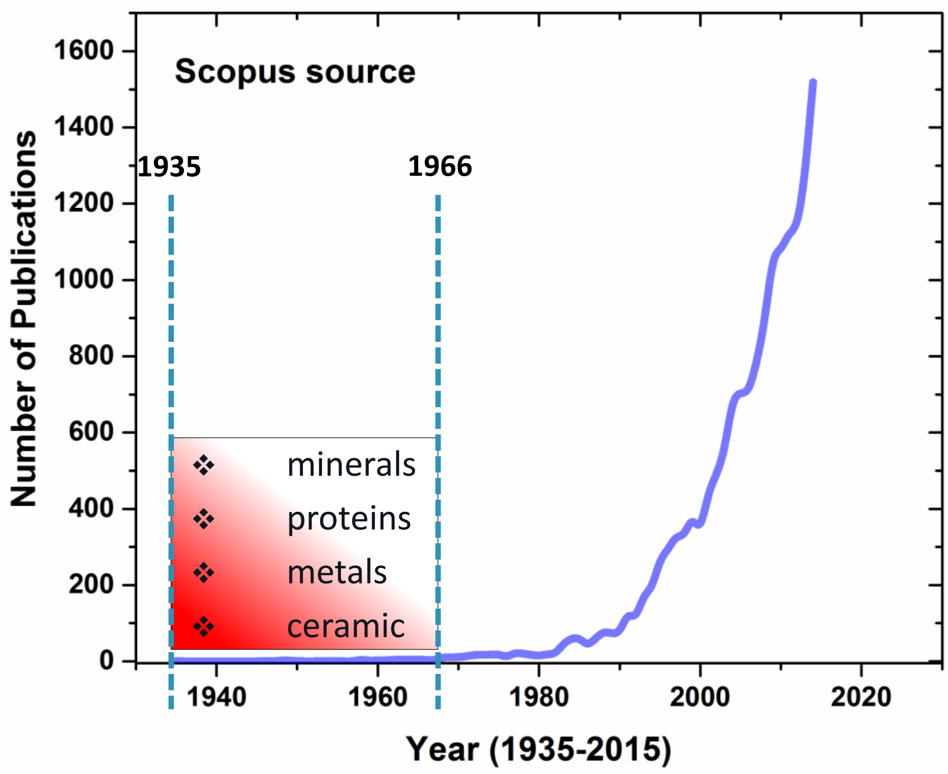
- Effect of Ball Milling



Ball milling: Historical development

ICARUS SUPERMAT

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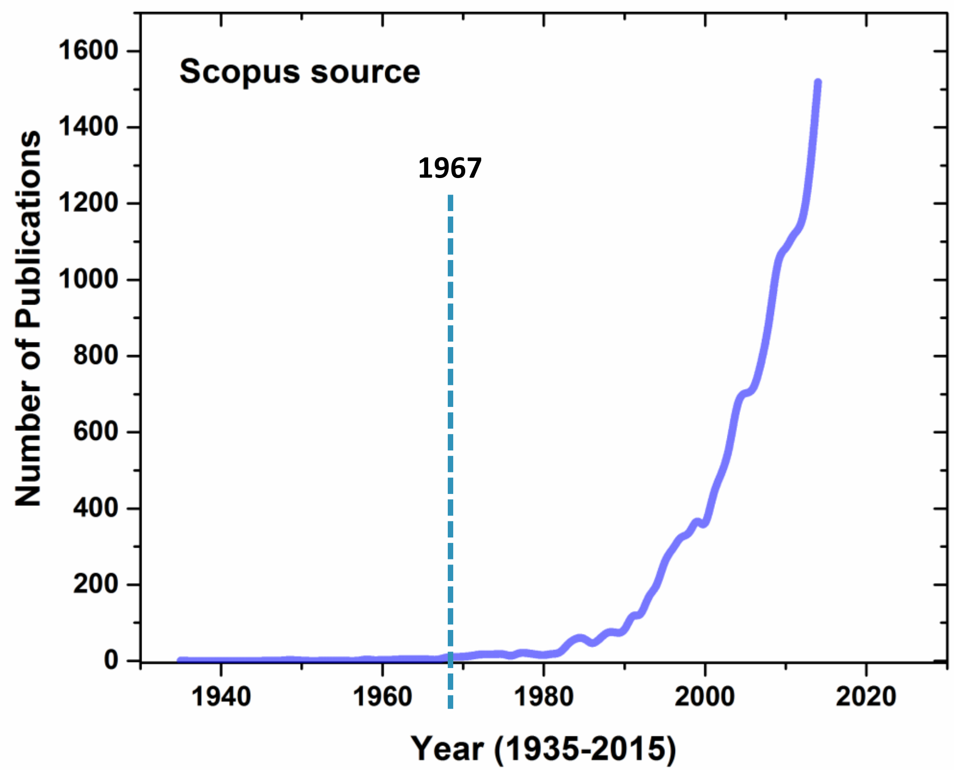
- <u>Synthesis of the 1° solid-solution</u>



ELSEVIER

Journal of Catalysis

Volume 8, Issue 2, June 1967, Pages 189-196

Solid solution formation in the $TiCl_3$-$AlCl_3$ system

E.G.M. Tornqvist, J.T. Richardson, Z.W. Wilchinsky, R.W. Looney

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Abstract

Solid solutions of $TiCl_3$ and $AlCl_3$ can be formed either directly by a cocrystallization reaction or by ball milling mixtures of $TiCl_3$ and $AlCl_3$ powers. The following evidence has been obtained for the presence of solid solutions: (a) X-ray diffraction shows only one phase which is isomorphous with $TiCl_3$; (b) the lattice parameters vary in a systematic manner with change in composition; (c) $AlCl_3$ cannot be easily sublimed from these preparations; and (d) the magnetic susceptibility dependence on temperature is the same for the ball-milled mixtures as for the cocrystallized preparations, but distinctly different from the nonmilled mixtures.

Solid solutions having structures isomorphous with γ-$TiCl_3$.

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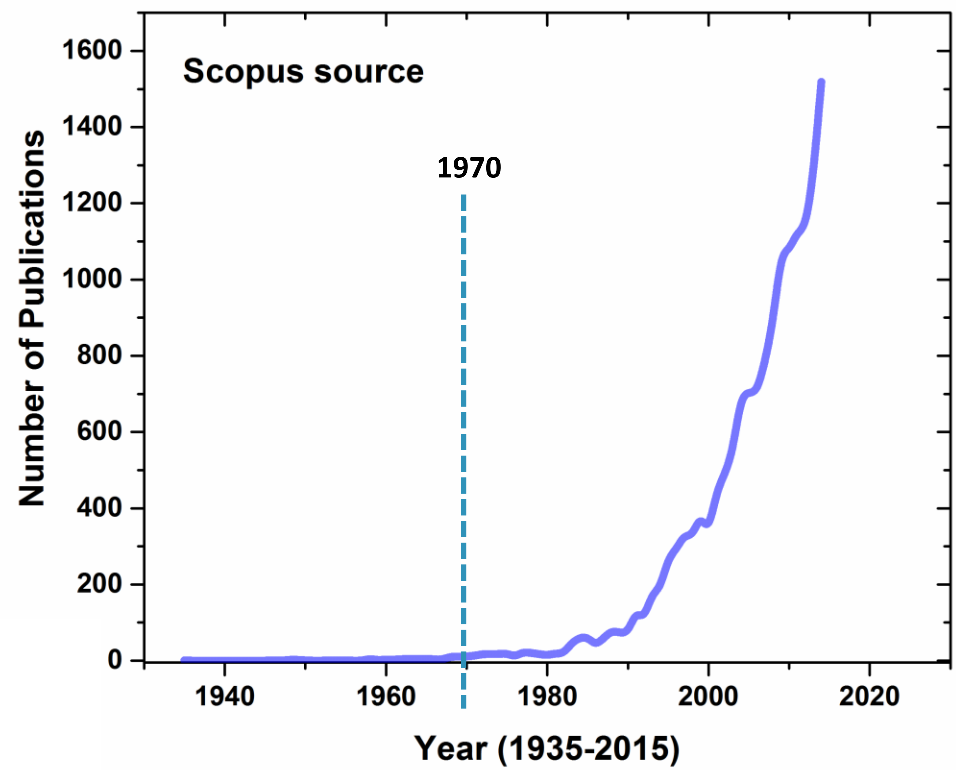
- Synthesis of the 1° solid-solution
- Synthesis of alloys by HE BM



Dispersion Strengthened Superalloys by Mechanical Alloying

JOHN S. BENJAMIN

A new process called "mechanical alloying" has been developed which produces homogeneous composite particles with an intimately dispersed, uniform internal structure. Materials formed by hot consolidation of this powder achieve the long-sought combination of dispersion strengthening and age-hardening in a high temperature alloy. While the process is amenable to making a variety of alloys, its first use has been to combine yttrium oxide and gamma prime hardening in a complex nickel-base superalloy. Typical stress rupture properties are 40,000 psi for 100 hr at 1400°F and 15,000 psi for 100 hr at 1900°F together with excellent sulfidation and cyclic oxidation resistance. From a fundamental standpoint, results show that the age-hardening dominates the low-temperature strength, dispersion strengthening dominates at high temperature, and the two are augmentative in the intermediate temperature range 1300° to 1500°F.

a new process «Mechanical Alloying»…….

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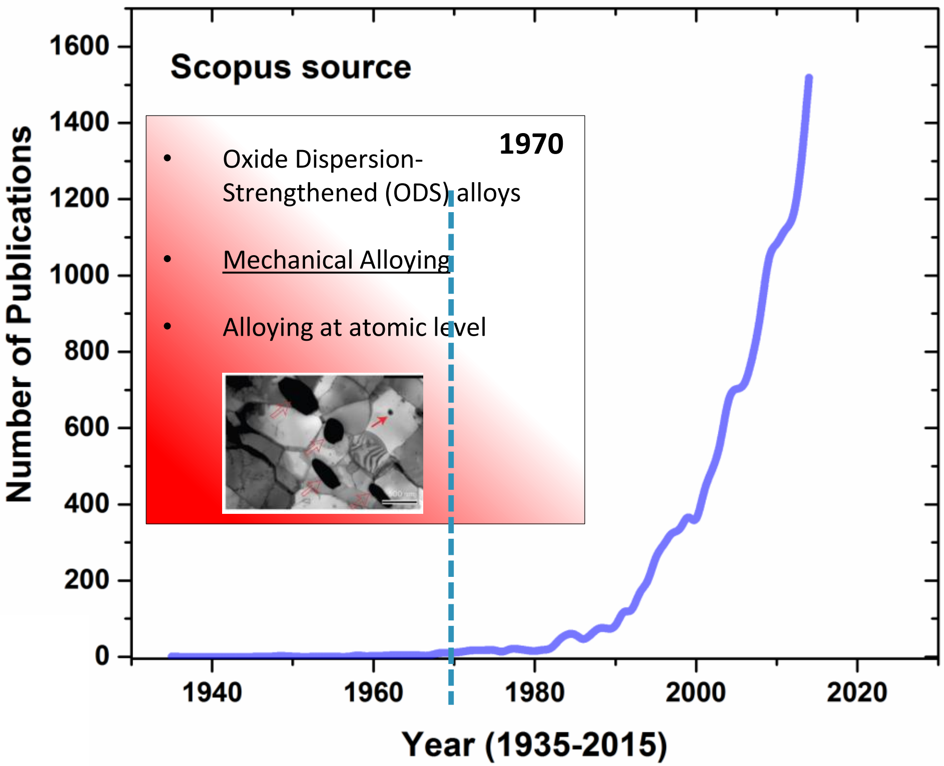

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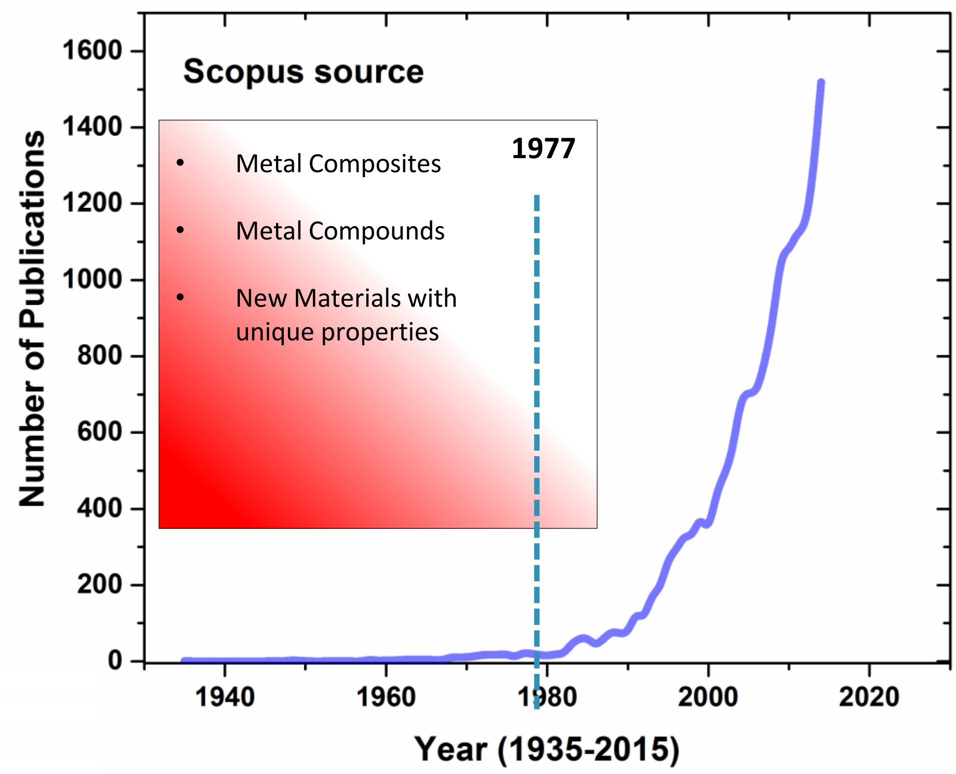

Dispersion Strengthened Aluminum Made by Mechanical Alloying

J. S. BENJAMIN AND M. J. BOMFORD

Dispersion strengthened aluminum with excellent combinations of electrical conductivity and tensile strength at room and elevated temperatures has been produced by mechanical alloying. The strength levels, obtained with only about 2.75 to 5.4 vol pct dispersoid (Al_2O_3 plus carbon), equal or surpass those of conventionally produced SAP containing 11.5 vol pct Al_2O_3. The electrical conductivity is considerably higher than that of SAP with comparable strength. It is concluded that these superior properties are due to a finer, more equiaxed dispersoid and a better dispersoid distribution than found in conventionally produced SAP.

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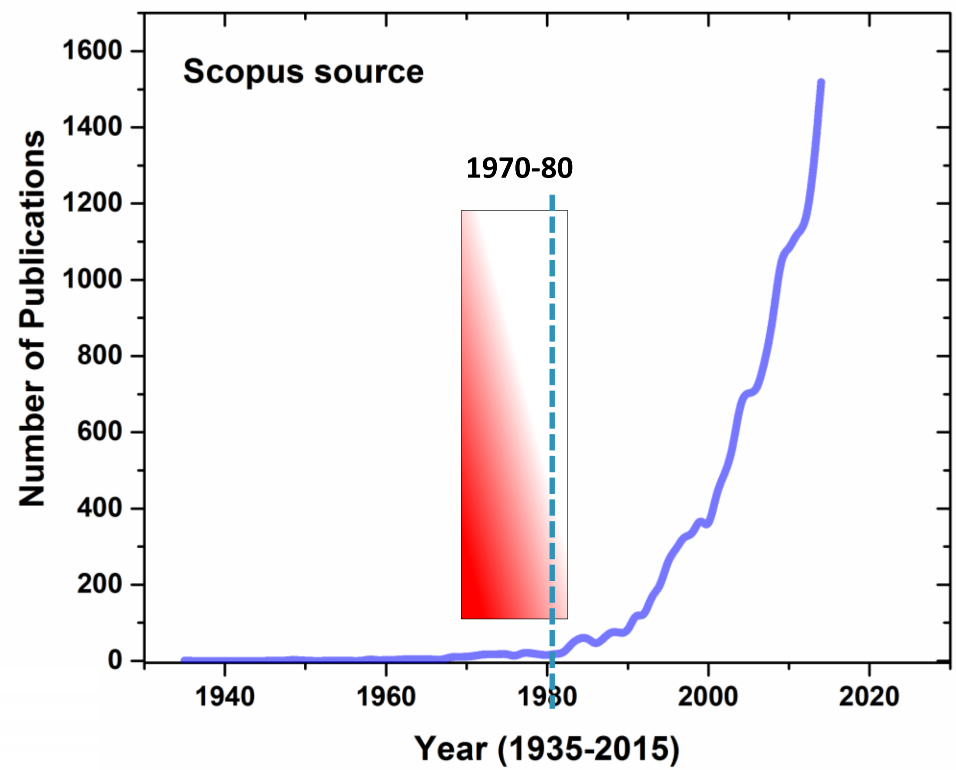

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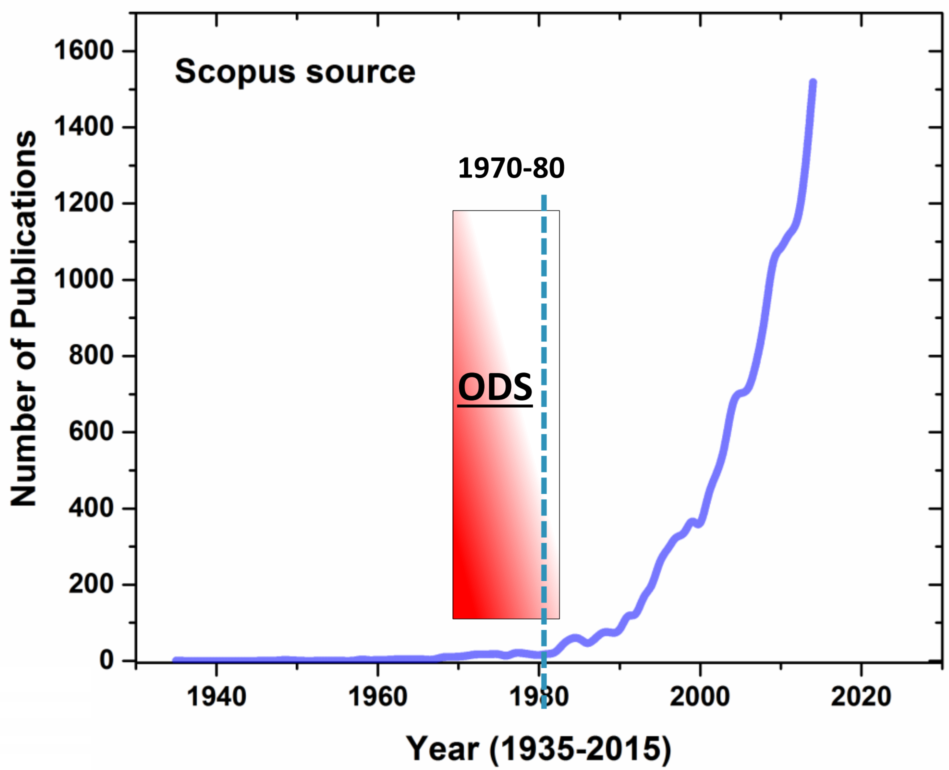

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Ball milling: Historical development

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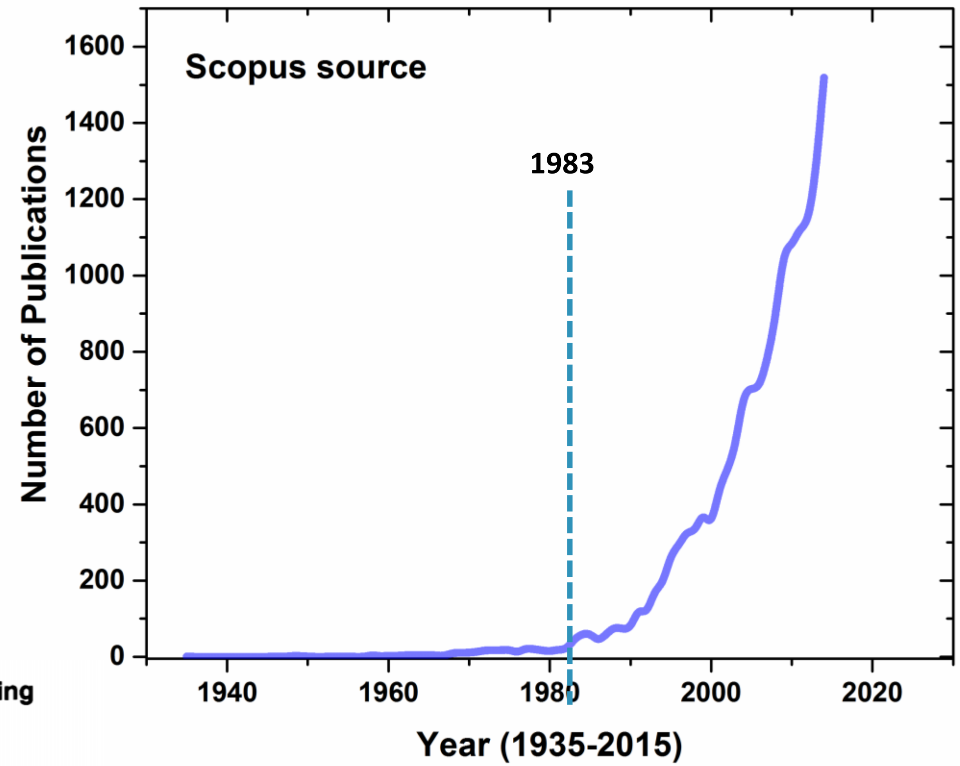
- Amorphous Alloys - Metallic Glasses



Preparation of "amorphous" $Ni_{60}Nb_{40}$ by mechanical alloying

C. C. Koch,[a] O. B. Cavin, C. G. McKamey, and J. O. Scarbrough

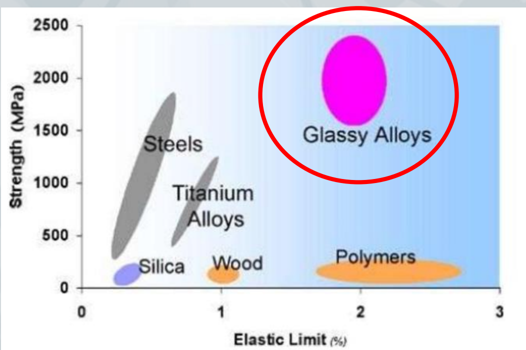
Metals and Ceramics Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830

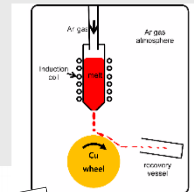
(Received 4 August 1983; accepted for publication 9 September 1983)

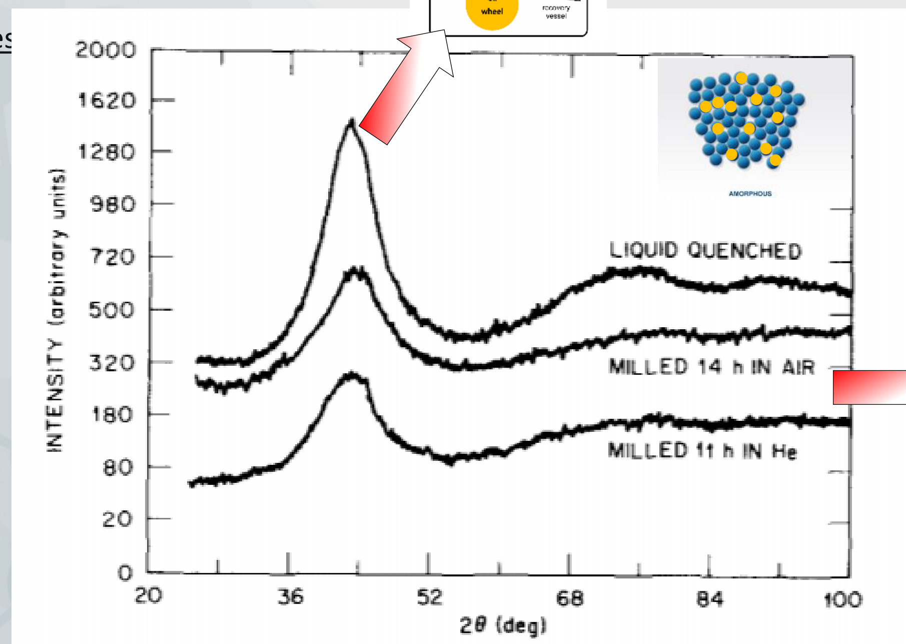
"Amorphous" $Ni_{60}Nb_{40}$ has been prepared by mechanical alloying of elemental nickel and niobium powders in a laboratory ball mill in controlled environments. X-ray diffraction was used to follow the progress of the mechanical alloying which eventually produced "amorphous" diffraction patterns similar to those for liquid quenched amorphous $Ni_{60}Nb_{40}$. Crystallization behavior was measured by differential scanning calorimetry for the mechanically alloyed and liquid quenched material. The differences that were observed in this behavior, and in the products of crystallization, may be attributed to impurities (especially oxygen) introduced during mechanical alloying.

Ball milling: Historical development

- Amorphous Alloys - Metallic Glasses



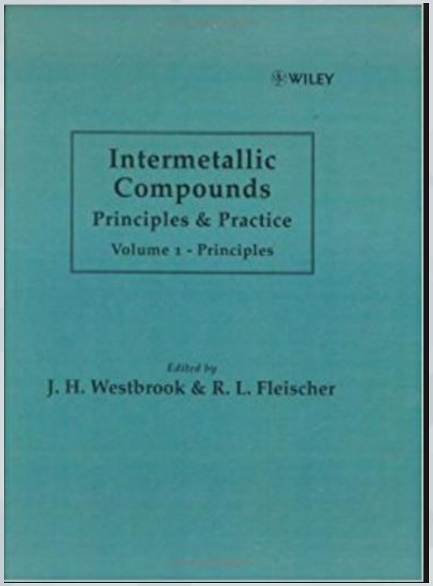




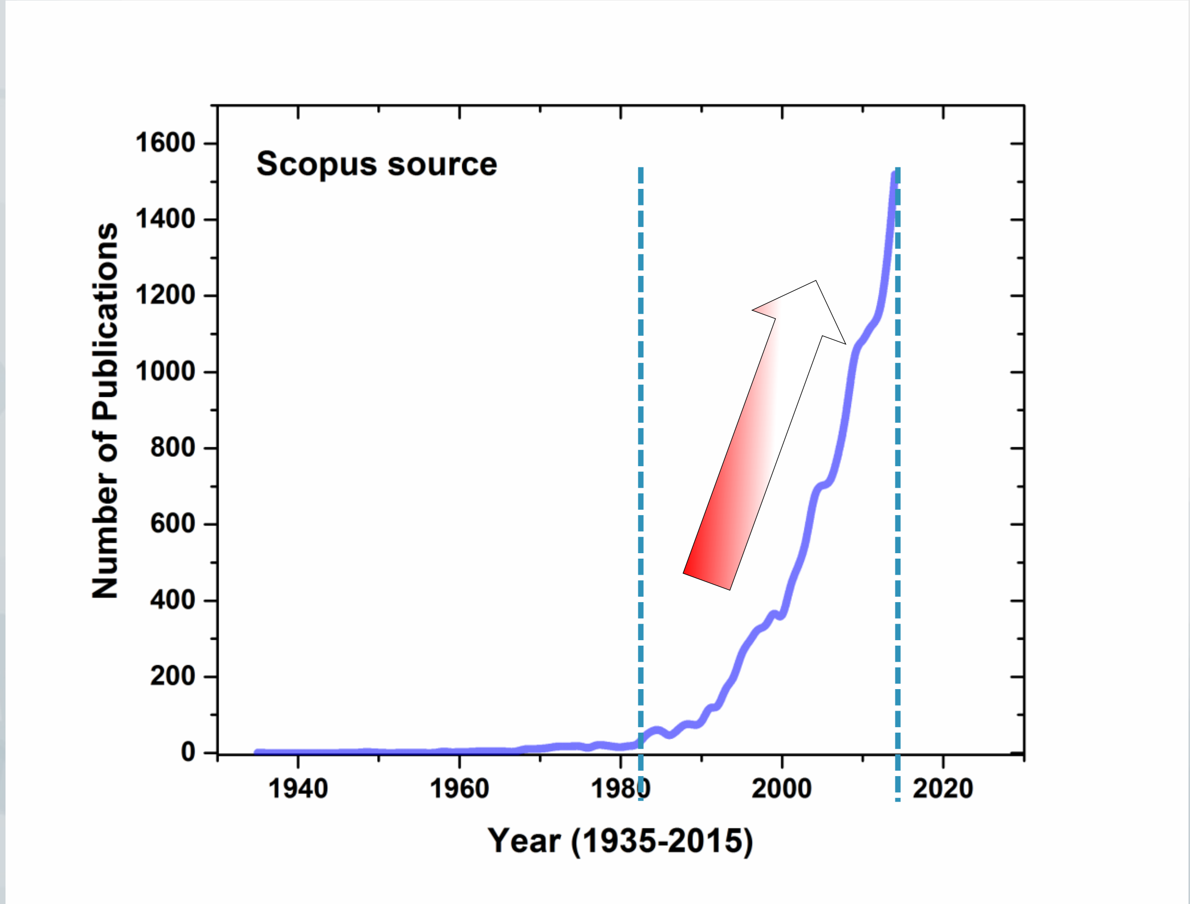
Solid State Amorphization (SSA)

Ball milling: Historical development

- Amorphous Alloys - Metallic Glass
- Nanocrystalline metals, alloys intermetallic compounds, ceramics, composites and nanocomposites



PL Martin and DA Hardwick




PERGAMON

Progress in Materials Science

Progress in Materials Science 46 (2001) 1–184
www.elsevier.com/locate/pmatsci

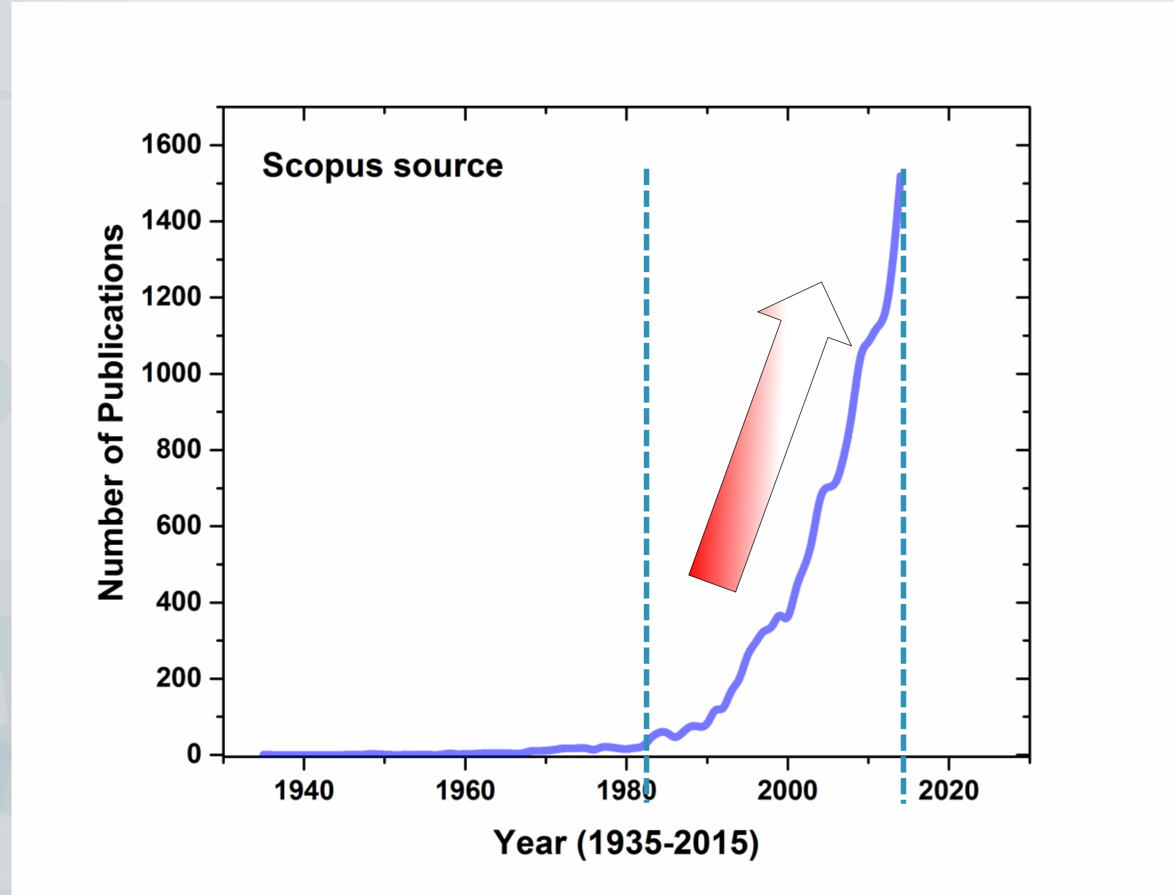
Mechanical alloying and milling

C. Suryanarayana

Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO 80401-1887, USA

Abstract

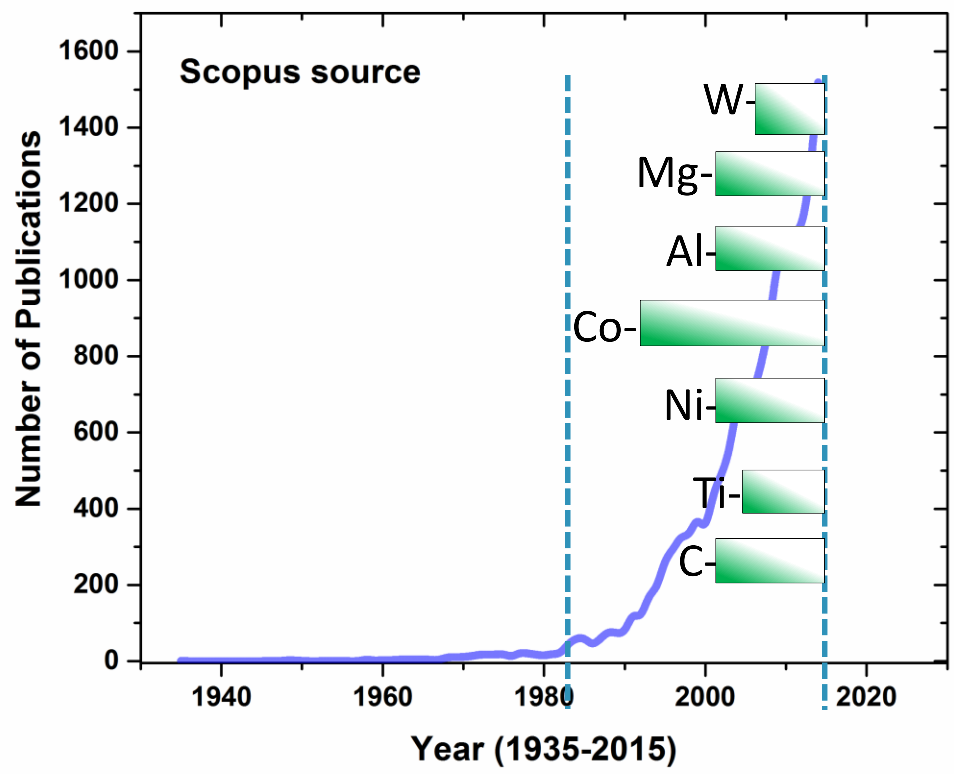
Mechanical alloying (MA) is a solid-state powder processng technique involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill. Originally developed to produce oxide-dispersion strengthened (ODS) nickel- and iron-base superalloys for applications in the aerospace industry, MA has now been shown to be capable of synthesizing a variety of equilibrium and non-equilibrium alloy phases starting from blended elemental or prealloyed powders. The non-equilibrium phases synthesized include supersaturated solid solutions, metastable crystalline and quasicrystalline phases, nanostructures, and amorphous alloys. Recent advances in these areas and also on disordering of ordered intermetallics and mechanochemical synthesis of materials have been critically reviewed after discussing the process and process variables involved in MA. The often vexing problem of powder contamination has been analyzed and methods have been suggested to avoid/minimize it. The present understanding of the modeling of the MA process has also been discussed. The present and potential applications of MA are described. Wherever possible, comparisons have been made on the product phases obtained by MA with those of rapid solidification processing, another non-equilibrium processing technique. © 2001 Elsevier Science Ltd. All rights reserved.



Ball milling as a non-equilibrium processing method

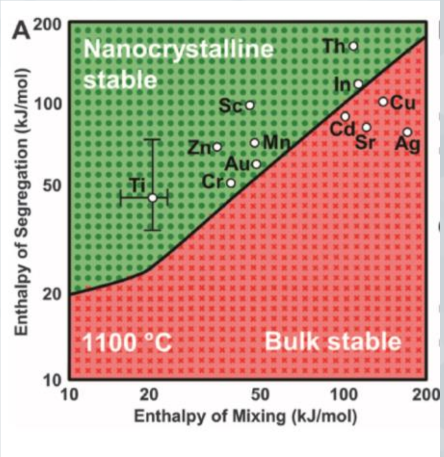
Ball milling: Historical development

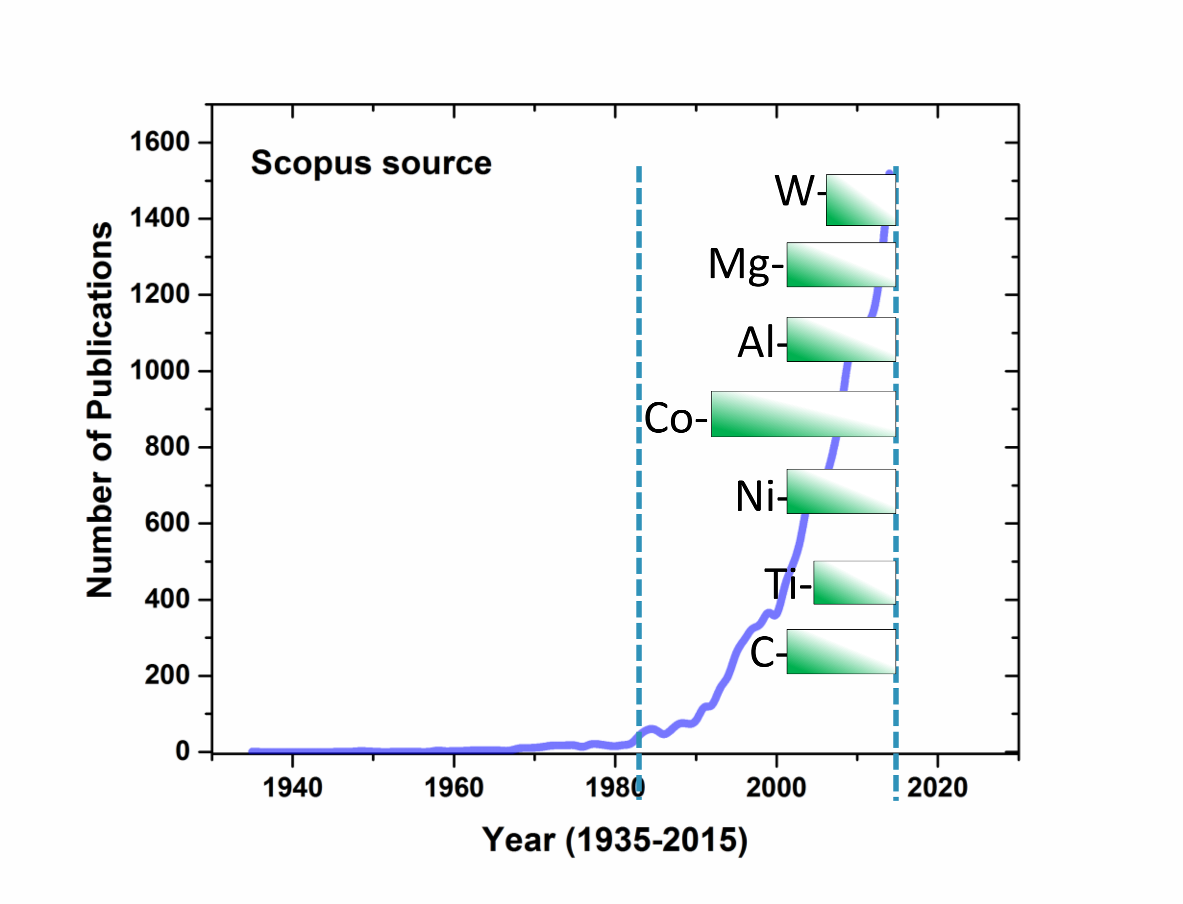
- Binary, thernary and multicomponents alloys



Ball milling: Historical development

- Binary, thernary and multicomponents alloys
- Stable Nanocrystalline Alloys





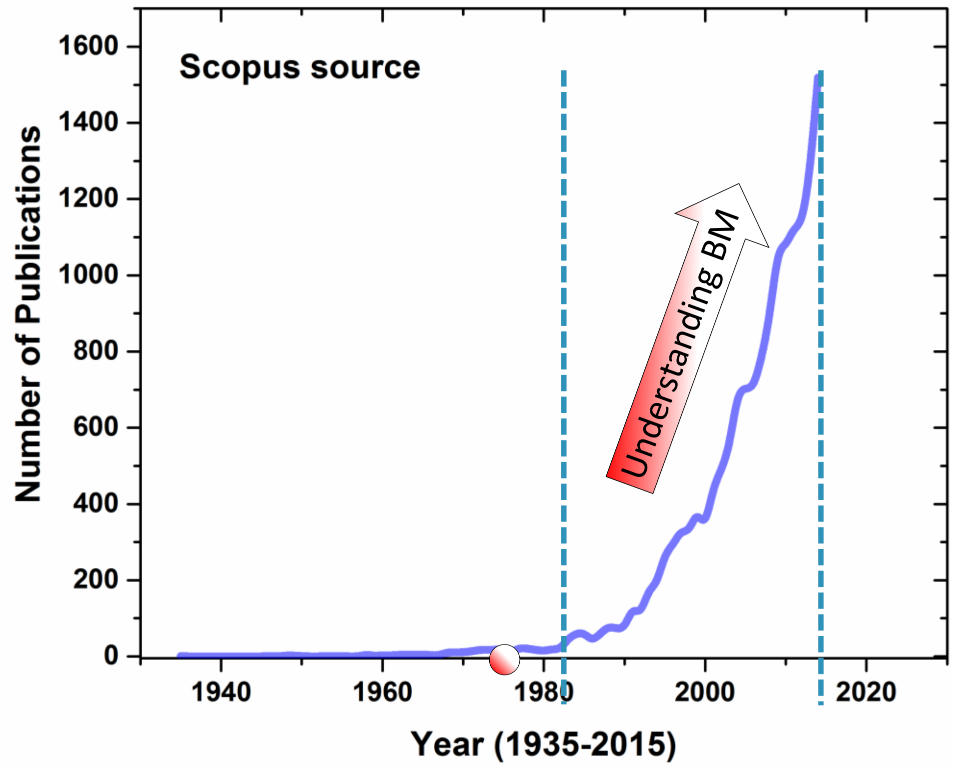
Tongjai Chookajorn, Heather A. Murdoch, Christopher A. Schuh, Design of Stable Nanocrystalline Alloys, Science 2012: 337, 951-954.

Ball milling: Historical development

The Mechanism of Mechanical Alloying

J. S. BENJAMIN AND T. E. VOLIN

The mechanical alloying process is a new method for producing composite metal powders with controlled microstructures. It is unique in that it is an entirely solid state process, permitting dispersion of insoluble phases such as refractory oxides and addition of reactive alloying elements such as aluminum and titanium. Interdispersion of the ingredients occurs by repeated cold welding and fracture of free powder particles. Refinement of structure is approximately a logarithmic function of time, and depends on the mechanical energy input to the process and work hardening of the materials being processed. A condition of steady state processing is eventually achieved marked by saturation (constant) hardness and constant particle size distribution, although structural refinement continues. Evidence of this is presented, and the nature of the cold welding and characteristics of the processed powder are described.



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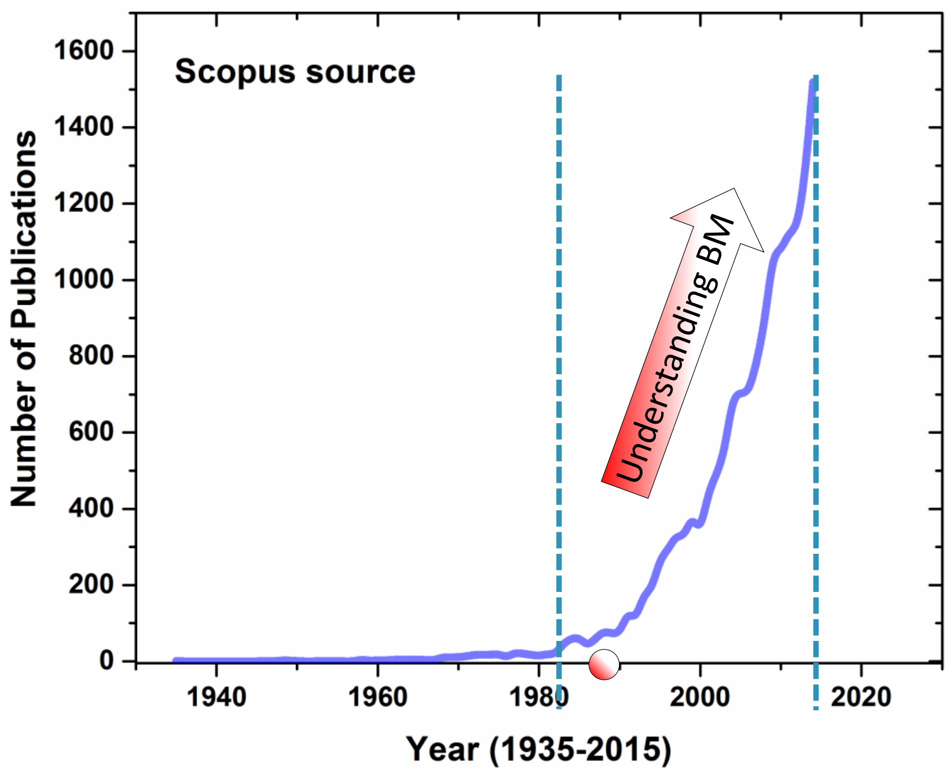
The Physics of Mechanical Alloying: A First Report

D.R. MAURICE and T.H. COURTNEY

In this paper, we present a first attempt to define the basic geometry, mechanics, and physics of the process of mechanical alloying. The geometry of the collision events which lead to particle fragmentation and coalescence is modeled on the basis of Hertzian contacts between the grinding media which entrap a certain amount of material volume between the impacting surfaces. This geometry essentially defines the volume of material affected per collision, and from this information and characteristics of the specific mill and the material being processed, impact times, powder strain rates and strains, powder temperature increase, powder cooling times, and milling times can be approximated.



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Ball milling: Historical development

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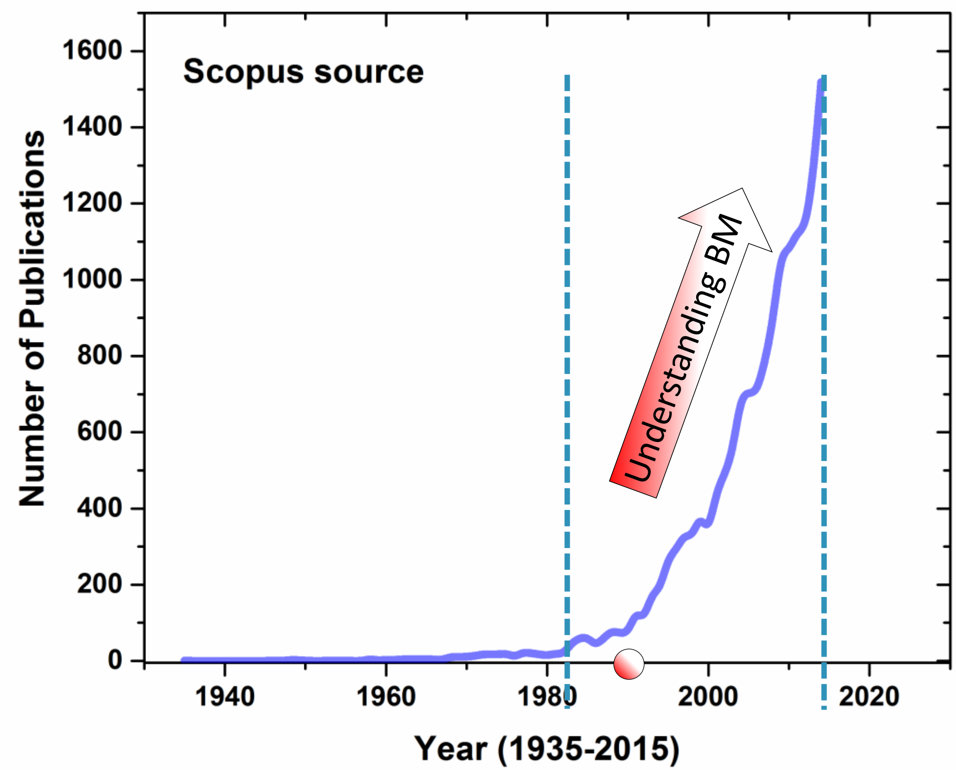
Mechanical Alloying of the Fe-Zr System.
Correlation between Input Energy and End Products.

N. BURGIO, A. IASONNA, M. MAGINI (*), S. MARTELLI and F. PADELLA
Amorphous Materials Project, TIB/ENEA, CRE
Casaccia, Via Anguillarese, Roma, Italia

(ricevuto il 21 Maggio 1990)



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The mechanical alloying process is a new method for producing composite metal powders with controlled microstructures. It is unique in that it is an entirely solid state process, permitting dispersion of insoluble phases such as refractory oxides and addition of reactive alloying elements such as aluminum and titanium. Interdispersion of the ingredients occurs by repeated cold welding and fracture of free powder particles. Refinement of structure is approximately a logarithmic function of time, and depends on the mechanical energy input to the process and work hardening of the materials being processed. A condition of steady state processing is eventually achieved marked by saturation (constant) hardness and constant particle size distribution, although structural refinement continues. Evidence of this is presented, and the nature of the cold welding and characteristics of the processed powder are described.

The Physics of Mechanical Alloying: A First Report

D.R. MAURICE and T.H. COURTNEY

In this paper, we present a first attempt to define the basic geometry, mechanics, and physics of the process of mechanical alloying. The geometry of the collision events which lead to particle fragmentation and coalescence is modeled on the basis of Hertzian contacts between the grinding media which entrap a certain amount of material volume between the impacting surfaces. This geometry essentially defines the volume of material affected per collision, and from this information and characteristics of the specific mill and the material being processed, impact times, powder strain rates and strains, powder temperature increase, powder cooling times, and milling times can be approximated.

Mechanical Alloying of the Fe-Zr System. Correlation between Input Energy and End Products.

N. BURGIO, A. IASONNA, M. MAGINI (*), S. MARTELLI and F. PADELLA

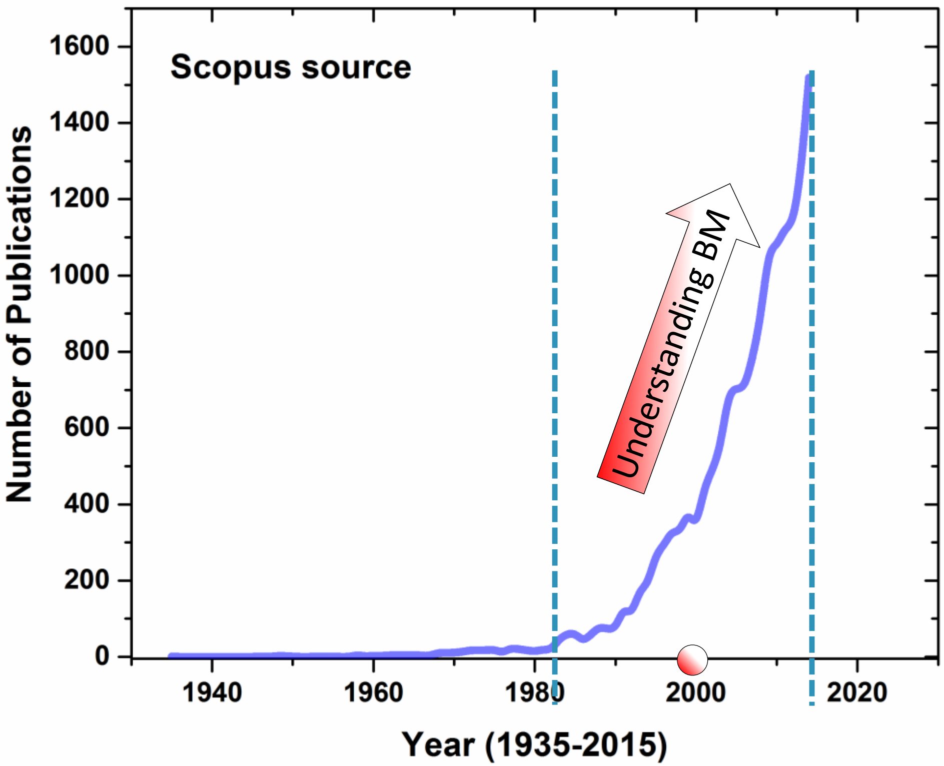
Amorphous Materials Project, TIB/ENEA, CRE Casaccia, Via Anguillarese, Roma, Italia

(ricevuto il 21 Maggio 1990)

Impact characteristics and mechanical alloying processes by ball milling: Experimental evaluation and modelling outcomes

F. Delogu et al.

Article in International Journal of Non-Equiulibrium Processing 11(3):235-269 · January 2000



Mechanism of mechanical alloying

Ball milling: Historical development

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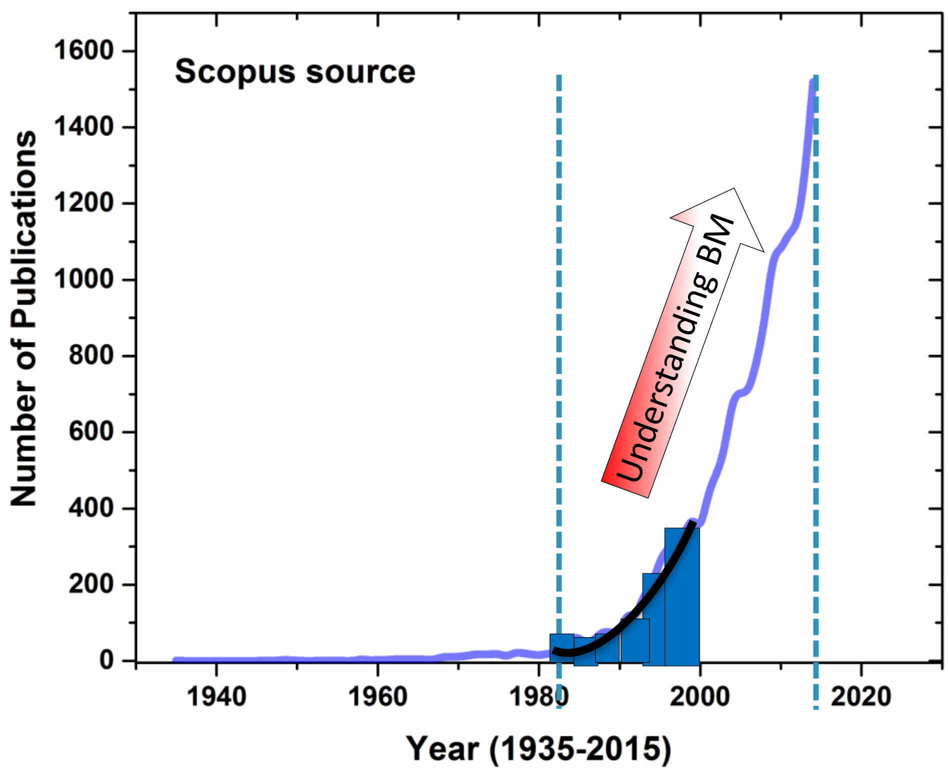
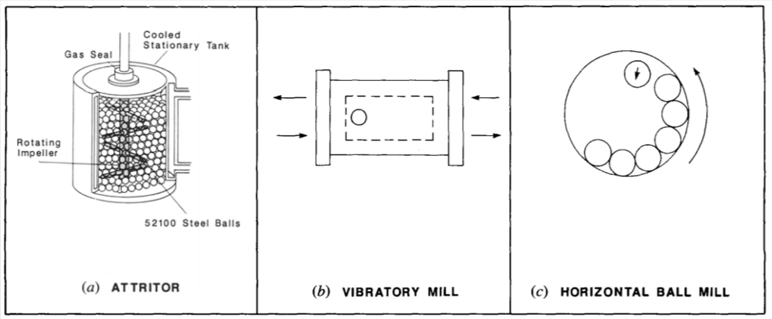
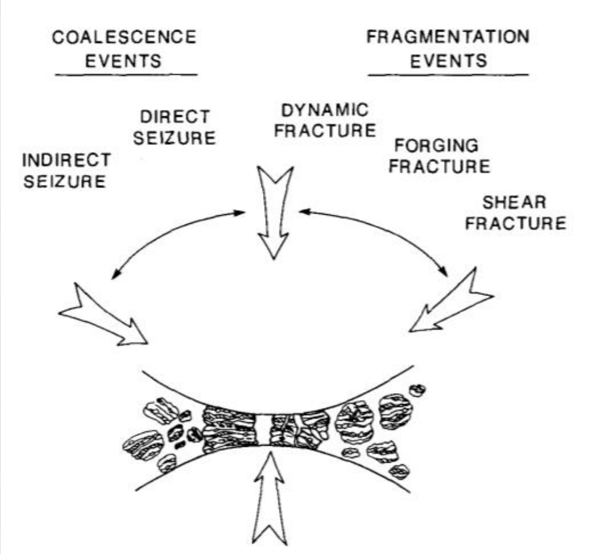


Mechanism of mechanical alloying

Ball milling: Process

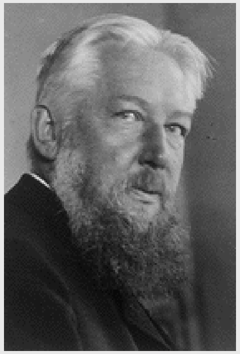
- Milling Parameters and Basic Process





D.R. MAURICE and T.H. COURTNEY, The Physics of Mechanical Alloying" A First Report, METALLURGICAL TRANSACTIONS A, VOLUME 21A, FEBRUARY 1990--289

- Friedrich Wilhelm Ostwald (2 September 1853 – 4 April 1932)
- Nobel Laureate in Chemistry - 1909
- In 1887, he coined the term "<u>mechanochemistry</u>", as a part of physical chemistry as thermochemistry, electrochemistry, or photochemistry



***Mechanochemistry** is the chemistry in which the thermodynamic state variables and functions of a given chemical system, including at least one solid phase, change in response to the effects of non-hydrostatic mechanical stresses, and of the resulting plastic strain.*

Mechanochemistry: a long history

- 3rd century BC - Theophrastus of Eresus – De Lapidibus (On Stones)

THEOPHRASTI
DE LAPIDIBVS
LIBER,
Ab ADRIANO TVRNEBO
Latinitate donatus.

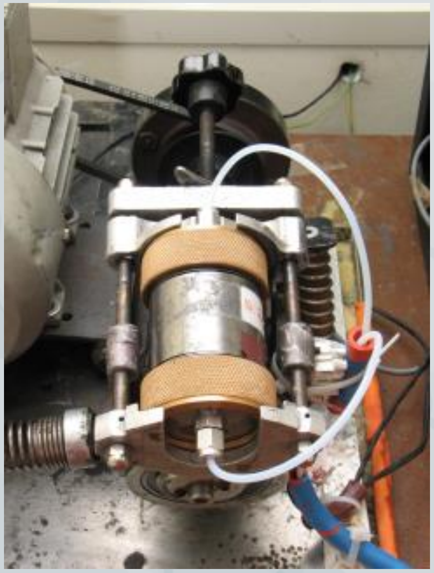
LVTETIÆ,
Ex Officina Federici Morelli Typographi Regij,
in vico Iacobęo, ad insigne Fontis.
M. D. LXXVIII.
CVM PRIVILEGIO REGIS.

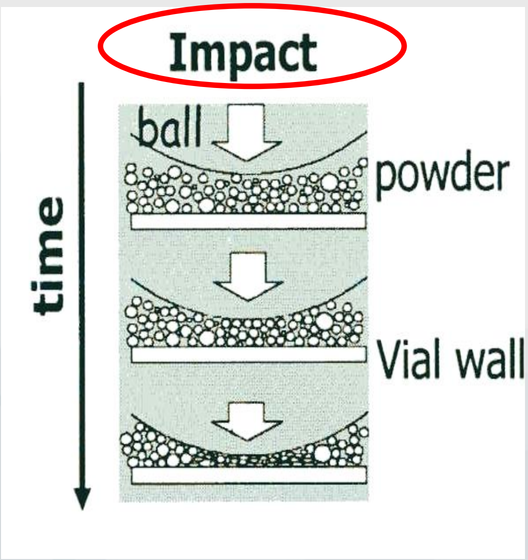
Reduction of Cinnabar

$$HgS + Cu \longrightarrow Hg + CuS$$

L. Takacs, The historical development of mechanochemistry, Chem. Soc. Rev., 2013, 42, 7649
F. Delogu, Fabrication of polymer nanocomposites via ball milling: Present status and future perspectives, Progress in Materials Science 86, 2017, 75–126

At impact…..

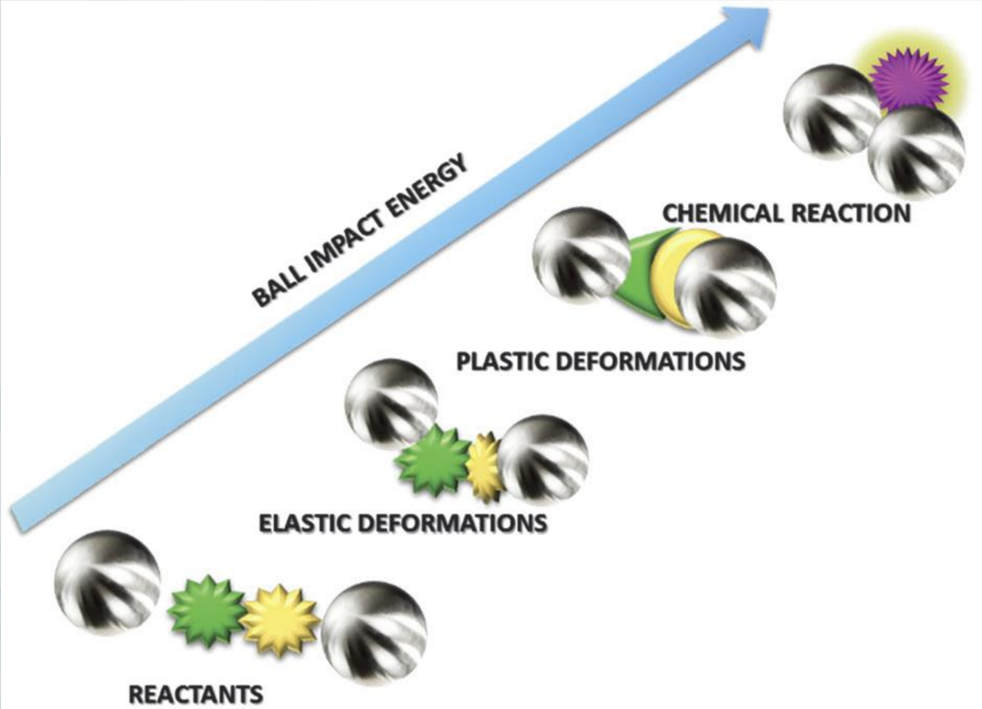




What about the process?

- D.L. Zhang, ***Prog. Mater. Sci.***, 2004, 49, 537
- F. Delogu, G. Cocco, ***Materials Science and Engineering***, 2003, 343, 314

At impact….



- C. Suryanarayana, ***Prog. Mater. Sci.,*** 2001, 46, 1
- C. Xu, S. De, A. M. Balu, M. Ojeda and R. Luque, ***Chem. Commun.,*** 2015,51, 6698

Investigation at different scale..

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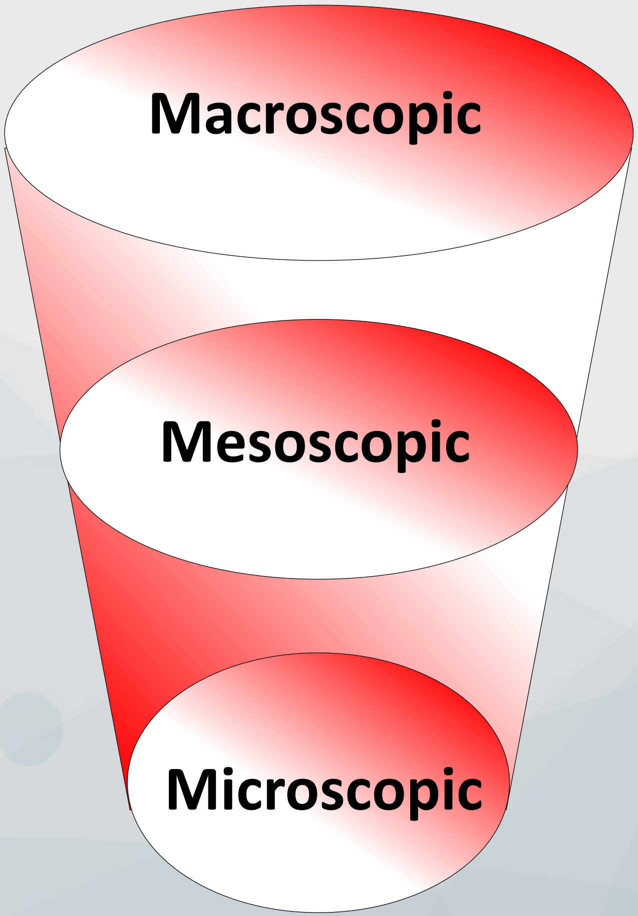
- Quantification of mechanochemical parameters on absolute scale
- Kinetics of the mechanochemical transformations and statistical approach
- Insight into atomistic processes



Into the Macroscopic scale..

- Quantification of mechanochemical parameters on absolute scale
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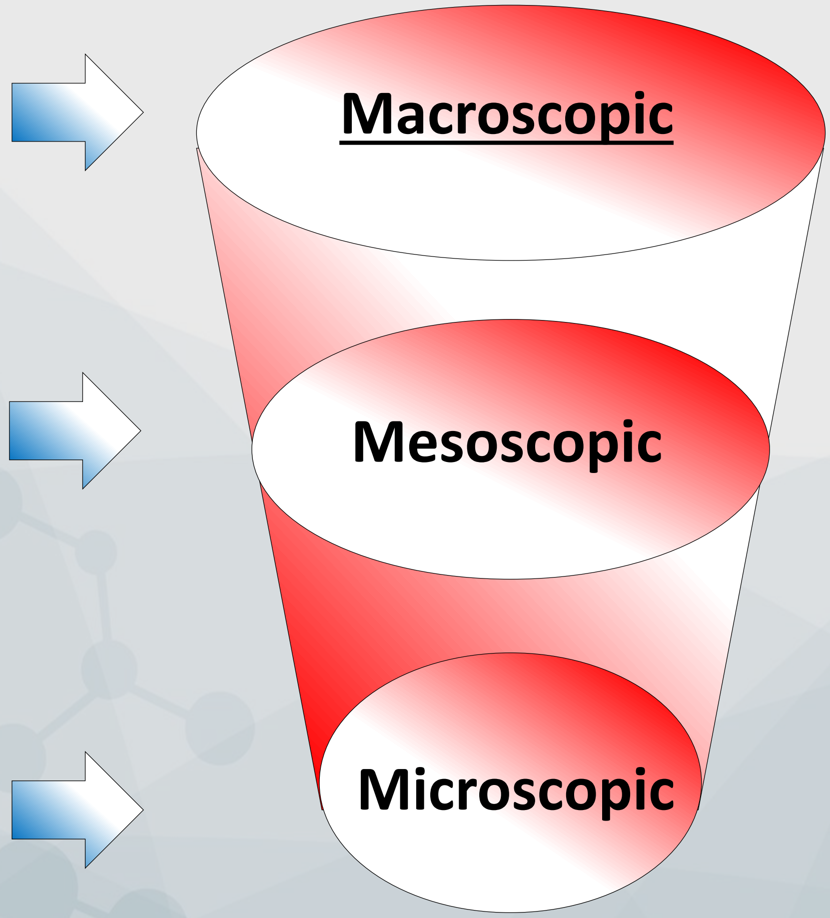
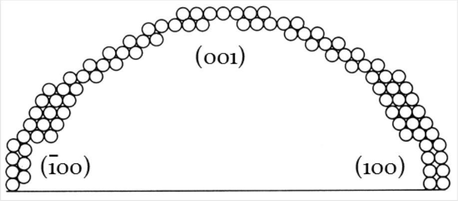
- Insight into atomistic processes



A quantitative approach

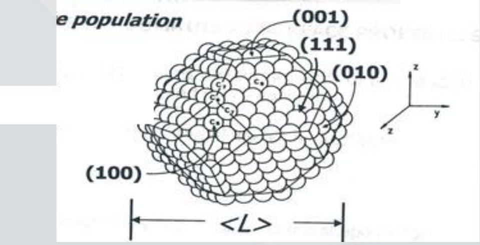
- **Surface chemistry**

Dissociative chemisorption properties (Geometric and Electronic Factors)



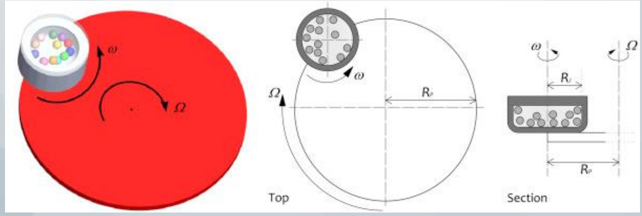
- **Microscture**

Well-established characterization routines for highly defective fine powders



- **Milling dynamics**

Control of the milling parameters



Parameters connected to milling intensity

Extensive Factor

Impact Energy, *E*

$$E\ [Joule] = \frac{1}{2} m (v_b + v_v)^2$$

Intensive Quantity

Collision Frequency, N_f

$$[hit\ s^{-1}]$$

Milling Intensity, $I = EN_f$

$$[Watt]$$

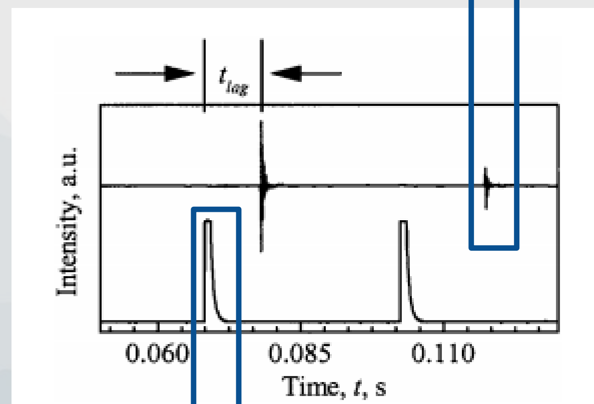
Ball-vial dynamics

$$E\,[Joule] = \frac{1}{2}m(v_b + v_v)^2$$

Magnetic sensor

Piezo transducer

Collision ball - flat base vial



Vial in extreme position

G. Cocco, F. Delogu, L. Schiffini, Journal of Materials Synthesis and Processing, 2000, 8, 167-180

For heterogeneous catalysis

Conventional Turnover Frequency

$$TF\left(\frac{mol}{at\,s}\right)=\frac{r}{m_p S_{sp} n_s}$$

A **Mechanochemical turnover Frequency**, **MTF**, can be obtained by considering the mass fraction processed at the impact, m_{hit} , and the impact frequency, N

$$MTF\left(\frac{mol}{at\,.\,hit}\right)=\frac{r}{m^{hit}_{p,i} S_{sp,i} n_{s,i}}\cdot\frac{1}{N}$$

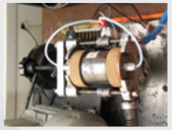
MTF gives the number of molecules transformed per hit per surface atom of the active phase, *i*

$$MT_E\left(\frac{mol}{at\,J}\right)=\frac{r}{m^{hit}_{p,i} S_{sp,i} n_{s,i}}\cdot\frac{1}{N}\cdot\frac{1}{E}$$

MT$_E$ is the instantaneous yield per surface atom of the active phase, *i*

G. Mulas, R. Campesi, S. Garroni, F. Delogu, C. Milanese, Applied Surface Science, 2011, 257, 8165-8170

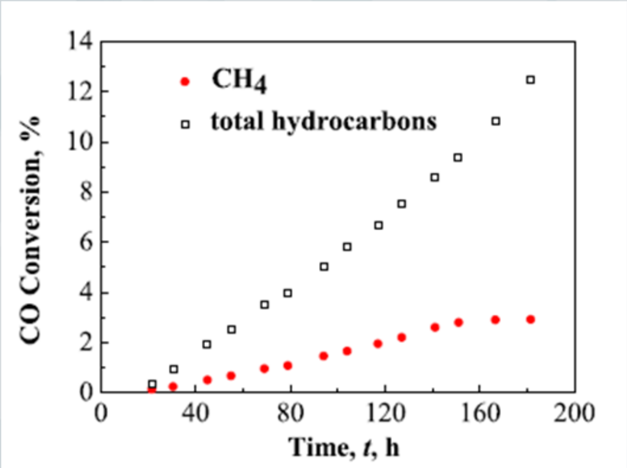
Synthesis FT on nanostructured FeCo



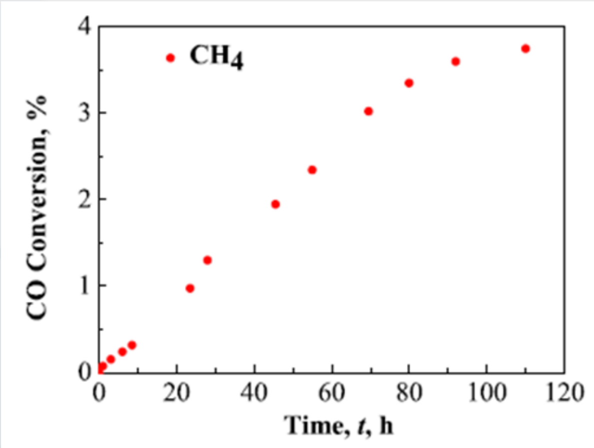
CO/H_2 → hydrocarbons

RT, FeCo

$(Fe_{50}Co_{50})$



$(Fe_{50}Co_{50})/TiO_2$



Mechanochemically induced FT reaction on FeCo catalysts showed high selectivity with respect to methane when FeCo powders were dispersed in TiO_2 support.

G. Mulas, R. Campesi, S. Garroni, F. Delogu, C. Milanese, Applied Surface Science, 2011, 257, 8165-8170

Synthesis FT on nanostructured FeCo

Sample	TOF $\left[\frac{\text{molecules}}{\text{atoms} \times \text{s}}\right]$	MTOF $\left[\frac{\text{molecules}}{\text{atoms} \times \text{hit}}\right]$	MT_E $\left[\frac{\text{molecules}}{\text{atoms} \times \text{J}}\right]$
$Fe_{50}Co_{50}$	3.44×10^{-6}	9.51×10^{-6}	0.14
$(FeCo)/(TiO_2)$	1.76×10^{-6}	4.8×10^{-2}	0.69

Mechanically Activated

MTOF
(300 K)

4.8×10^{-2}

Thermically Activated

TOF
(400 K)

13.8×10^{-3}

MTOF is of the same order of magnitude of TOF measured for the similar system activated by thermal treatment

G. Mulas, R. Campesi, S. Garroni, F. Delogu, C. Milanese, Applied Surface Science, 2011, 257, 8165-8170

Into the Mesoscopic scale…

- Quantification of mechanochemical parameters on absolute scale
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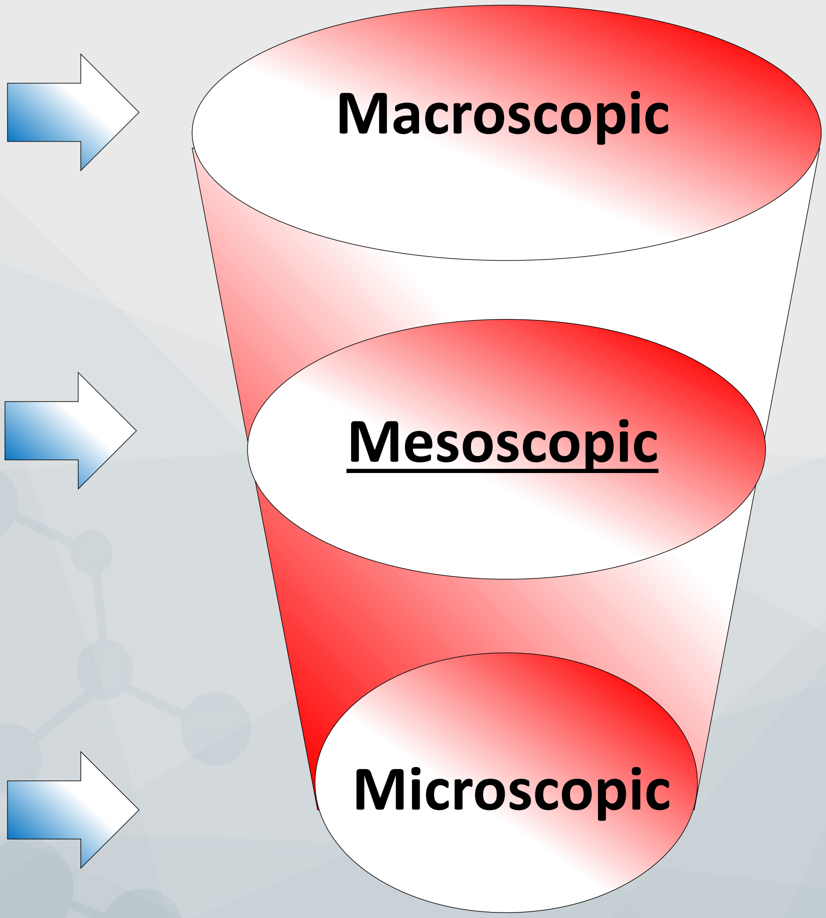

Into the Mesoscopic scale…

Why is so difficult to gain experimental insight into mesoscopic scale?

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Journal of Materials Science

Mechanically activated metathesis reaction in NaNH2-MgH2 powder mixtures

--Manuscript Draft--

Manuscript Number:	JMSC-D-17-00792R1
Full Title:	Mechanically activated metathesis reaction in NaNH2-MgH2 powder mixtures
Article Type:	Special: Mechanochemical Synthesis
Keywords:	Mechanochemistry; ball milling; kinetic model; metathesis reaction; hydrides.
Corresponding Author:	Sebastiano Garroni, Researcher Universidad de Burgos Burgos, SPAIN

Into the Mesoscopic scale…

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Journal of Materials Science

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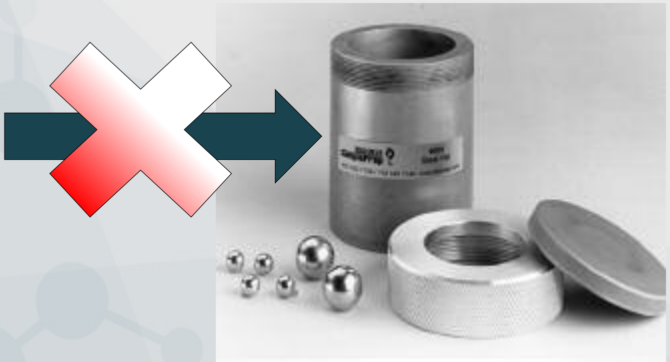
Keywords:	Mechanochemistry; ball milling; kinetic model; metathesis reaction; hydrides.
Corresponding Author:	Sebastiano Garroni, Researcher Universidad de Burgos Burgos, SPAIN

No real information about mechanism of reaction: crystal 1 + crystal 2 = crystal 3 + crystal 4. For instance, what is a mechanism of mass transfer?

Into the Mesoscopic scale…

How can we characterize the mechanism of the mechanically induced reaction?

Into the Mesoscopic scale…



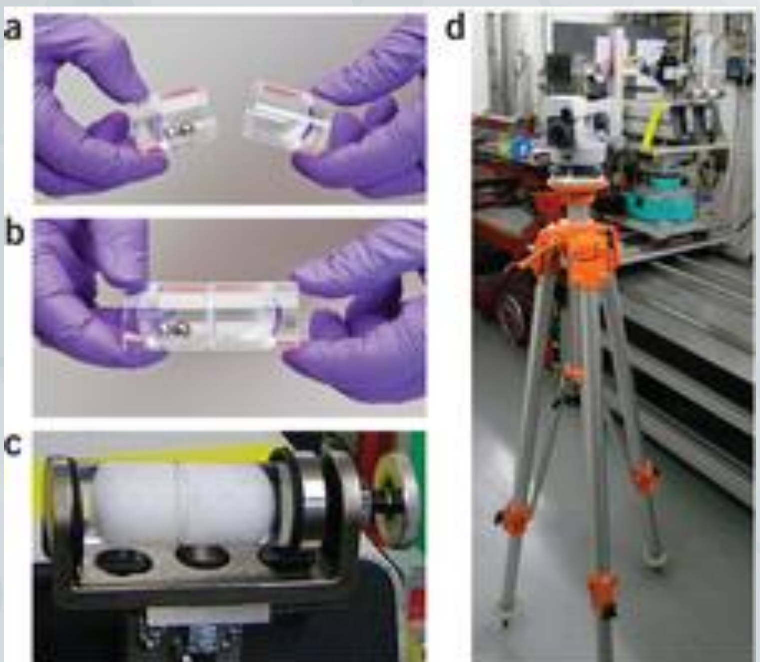
Stainless steel

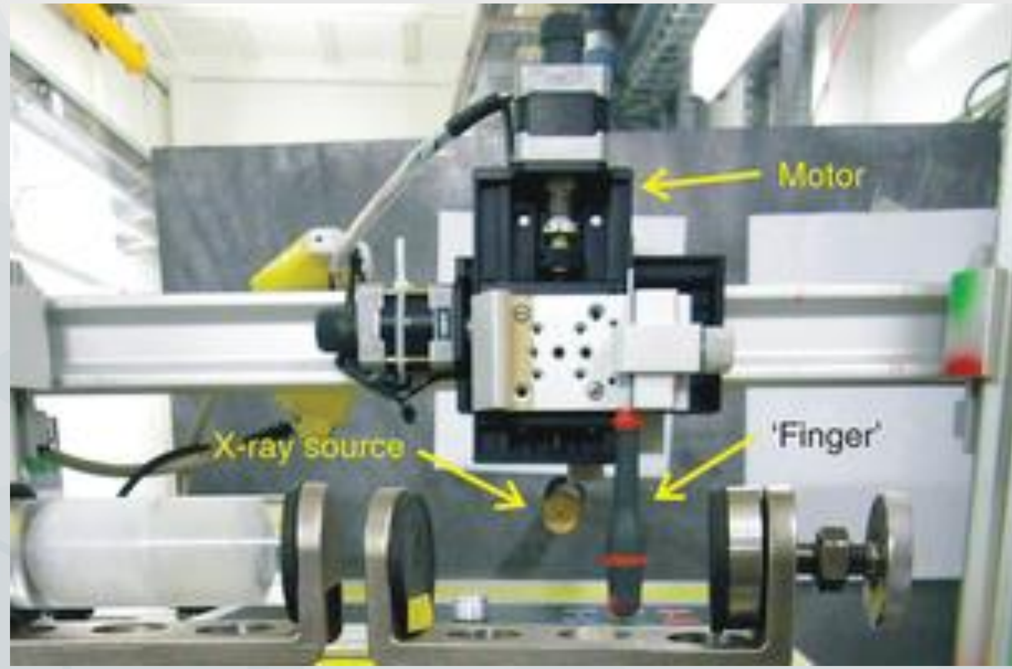
Into the Mesoscopic scale…

Stainless steel

Quartz

Into the Mesoscopic scale…





NATURE PROTOCOLS | PROTOCOL

In situ and real-time monitoring of mechanochemical milling reactions using synchrotron X-ray diffraction

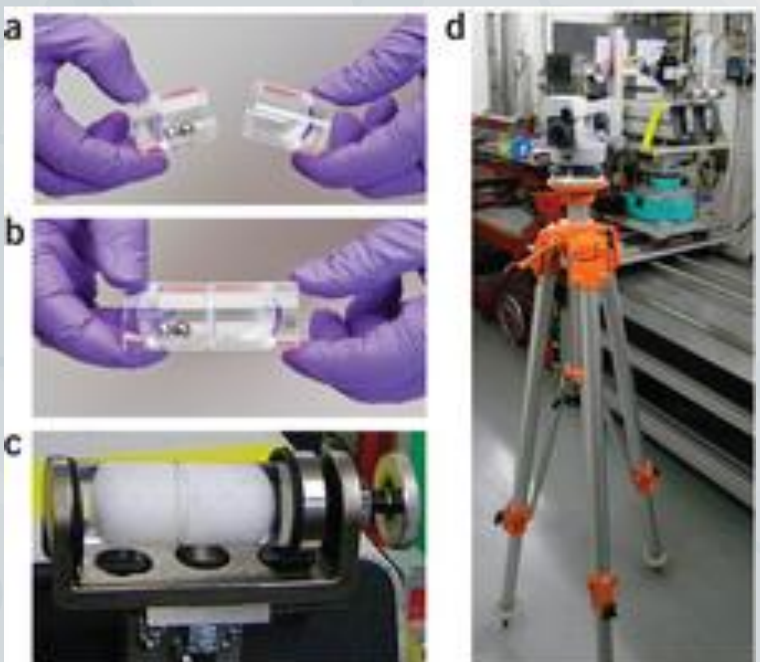
Ivan Halasz Simon A J Kimber Patrick J Beldon Ana M Belenguer Frank Adams Veijo Honkimäki Richard C Nightingale Robert E Dinnebier Tomislav Friščić

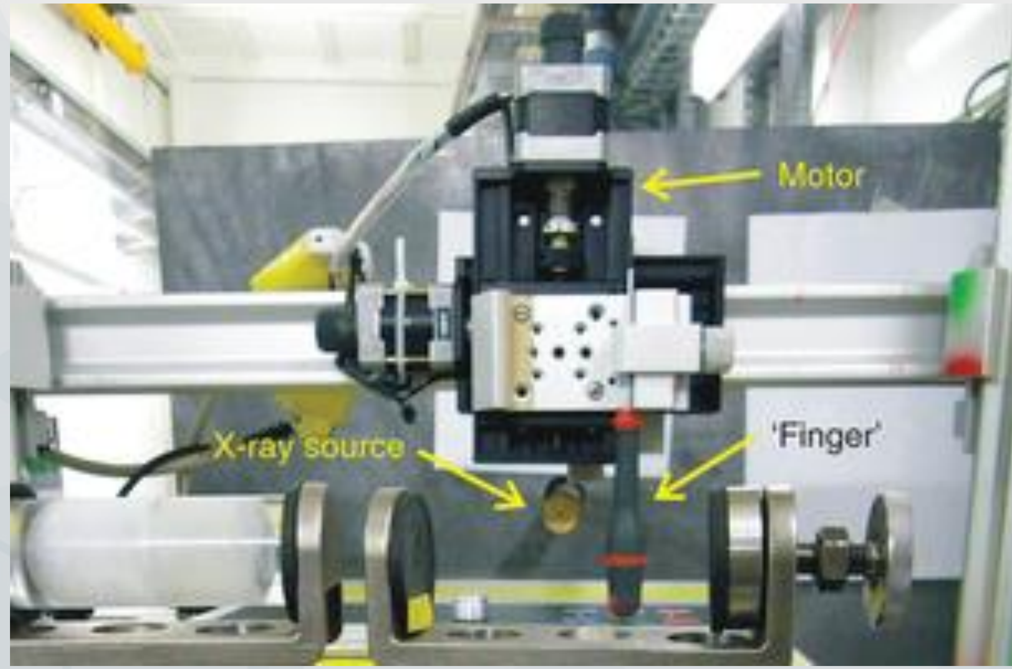
Affiliations | Contributions | Corresponding author

Nature Protocols **8**, 1718–1729 (2013) | doi:10.1038/nprot.2013.100
Published online 15 August 2013

Into the Mesoscopic scale…

This protocol results good for achieving macroscopic mechanism





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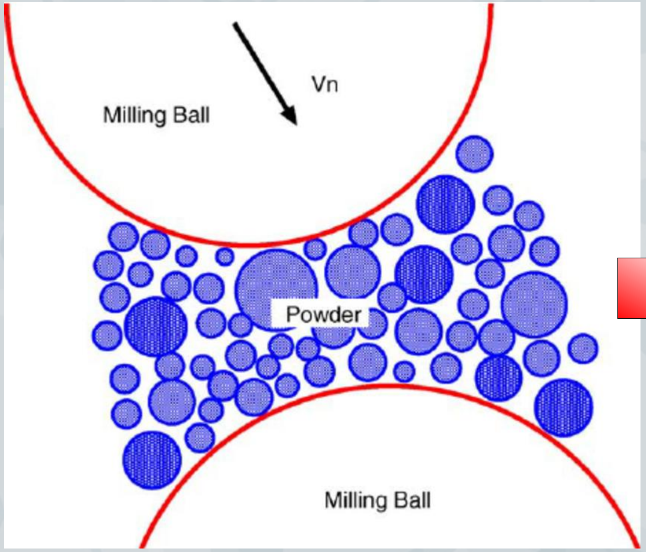
Into the Mesoscopic scale…

Since these species are quite lightweight, we have to push our experiments to the femtosecond time scale. Furthermore…..



- Powder trapped at each collision: 0.1 mg
- Powder involved in trasformation: 0.34%

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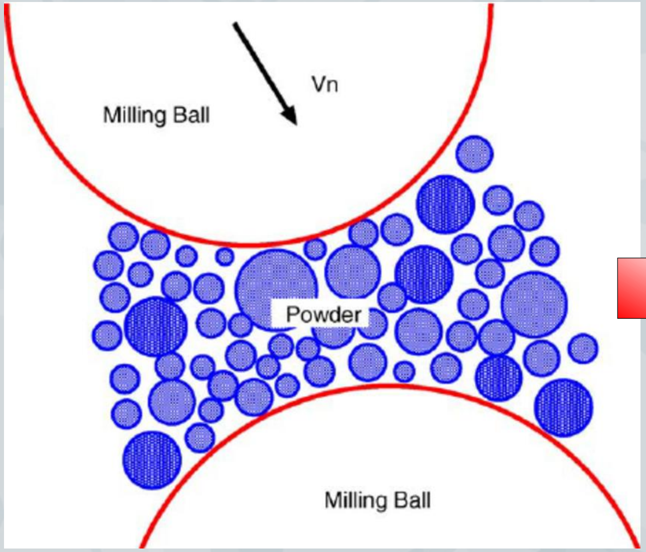

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Also for the most expert scientist in TEM characterization could be impossible to find 0.00034 mg in 8 g of powders.

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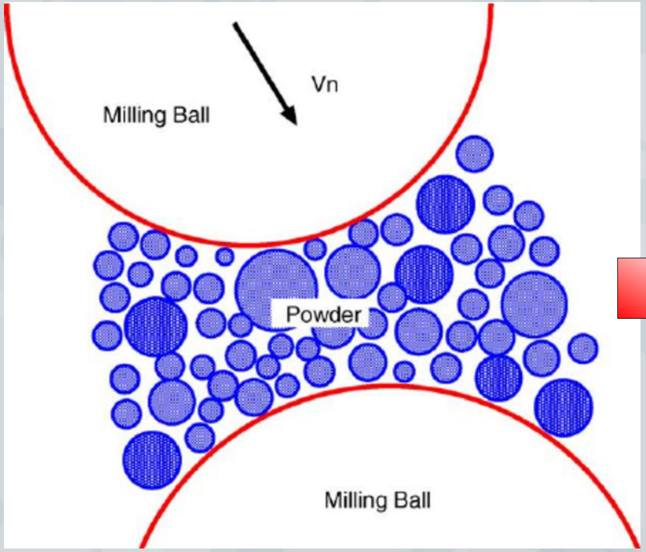
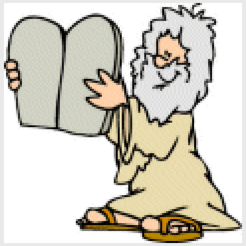


- Powder trapped at each collision: 0.1 mg
- Powder involved in trasformation: 0.34%

Also for the most expert scientist in TEM characterization could be impossible to find 0.00034 mg in 8 g of powders. Be patient!

Kinetic Model: "five commandments"



- Collisions are randomly distributed over the whole powder charge
- A small fraction of the powder charge is involved in each collision
- Powders are perfectly homogenized after each collision.
- Phase transformations occur on a fraction of the trapped powders as a result of the mechanical deformation processes associated to the collisions
- Times of the order of the collision duration are required for the phase transformations to occur

Kinetic model: equations

$$d\,\chi_o(n) = -k\,\chi_o(n)dn$$

Mass fractions never impacted

$$d\,\chi_i(n) = -k\,\chi_i(n)dn + \mathrm{k}\,\chi_{i-1}(n)dn$$

Mass fractions impacted once, χ_1, twice, χ_2, ……

- F. Delogu, G. Cocco, ***Materials Science and Engineering***, 2003, 343, 314

Kinetic model: equations

$$d\,\chi_o(n) = -k\,\chi_o(n)dn \quad \Rightarrow \quad \chi_o(n) = e^{-kn}$$

Mass fractions never impacted

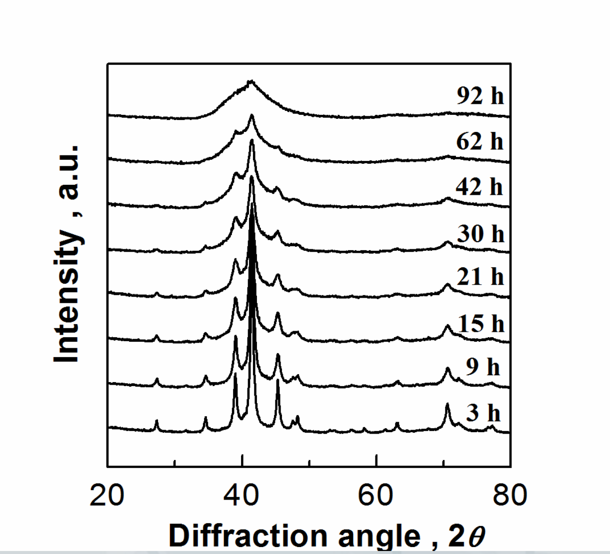
$$d\,\chi_i(n) = -k\,\chi_i(n)dn + \mathrm{k}\,\chi_{i-1}(n)dn \quad \Rightarrow \quad \chi_i(n) = [(kn)^i\,/i!] \quad e^{-kn}$$

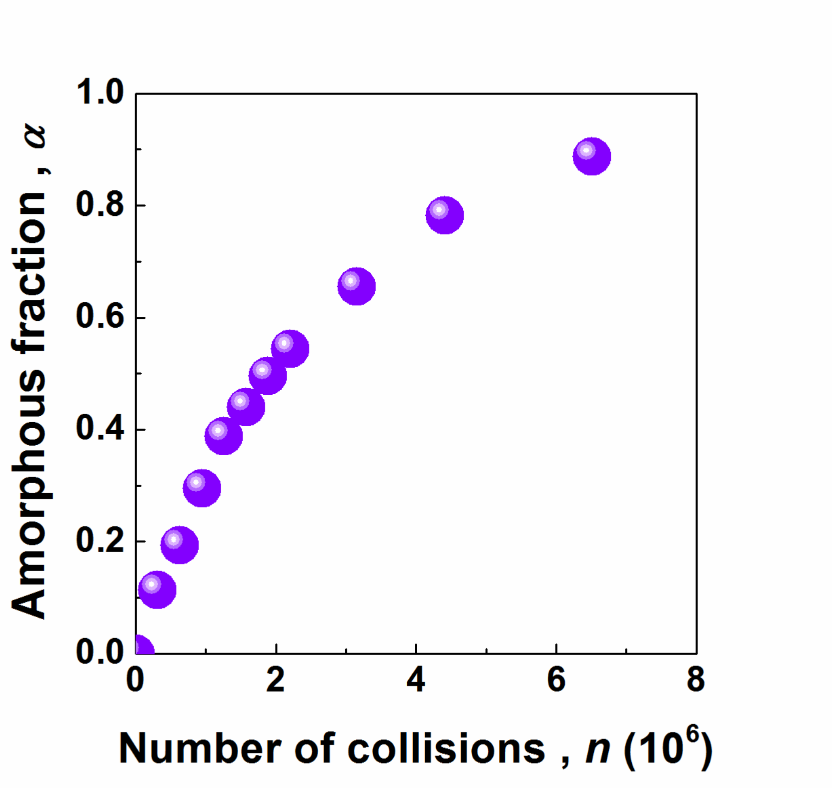
Mass fractions impacted once, χ_1, twice, χ_2, ……

k represents the phenomelogical rate constant referred to the number of impacts ***n*** for the given transformation process

- F. Delogu, G. Cocco, ***Materials Science and Engineering***, 2003, 343, 314

Case study: amorphization of $NiTi_2$





F. Delogu,, G. Cocco, Materials Science and Engineering A, 2003, A343, 314-317

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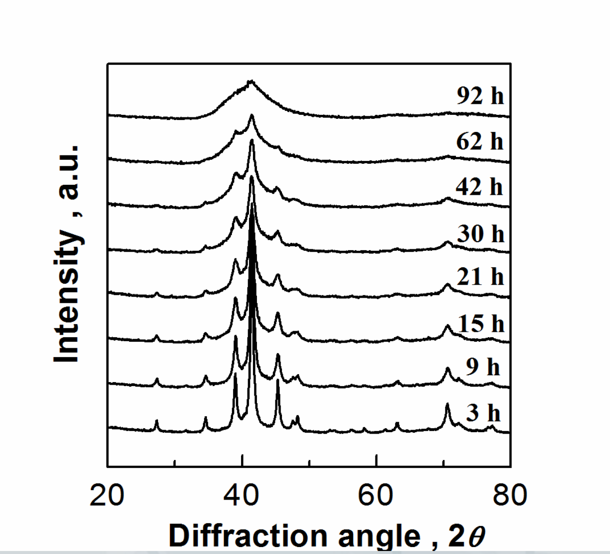
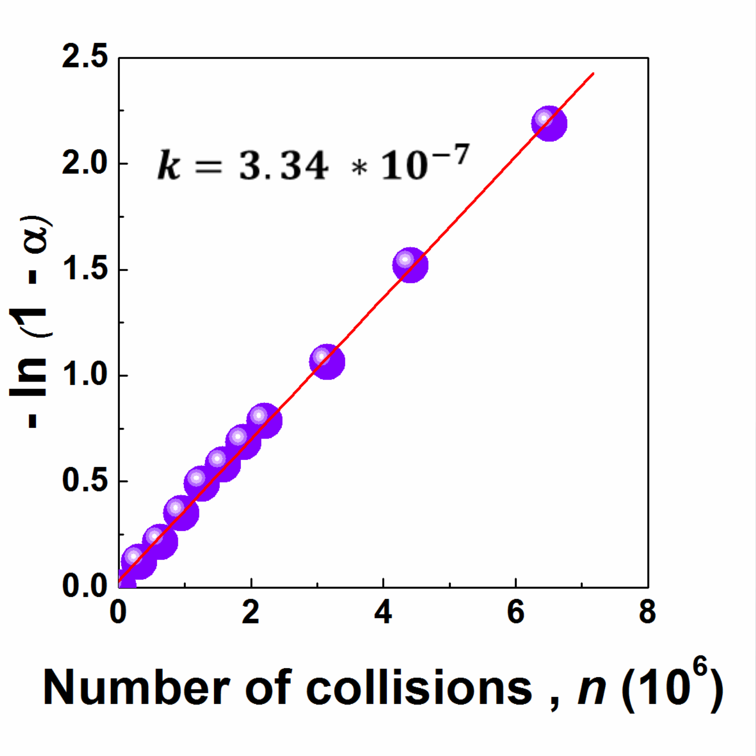


$$\chi_i(n) = [(kn)^i \,/ i!] \quad e^{-kn}$$



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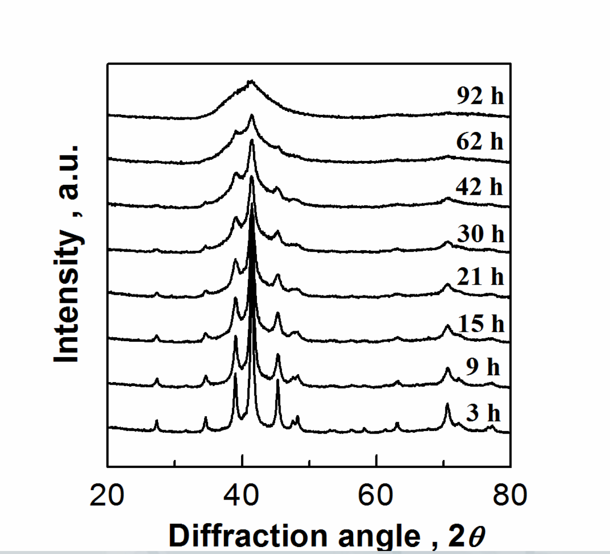

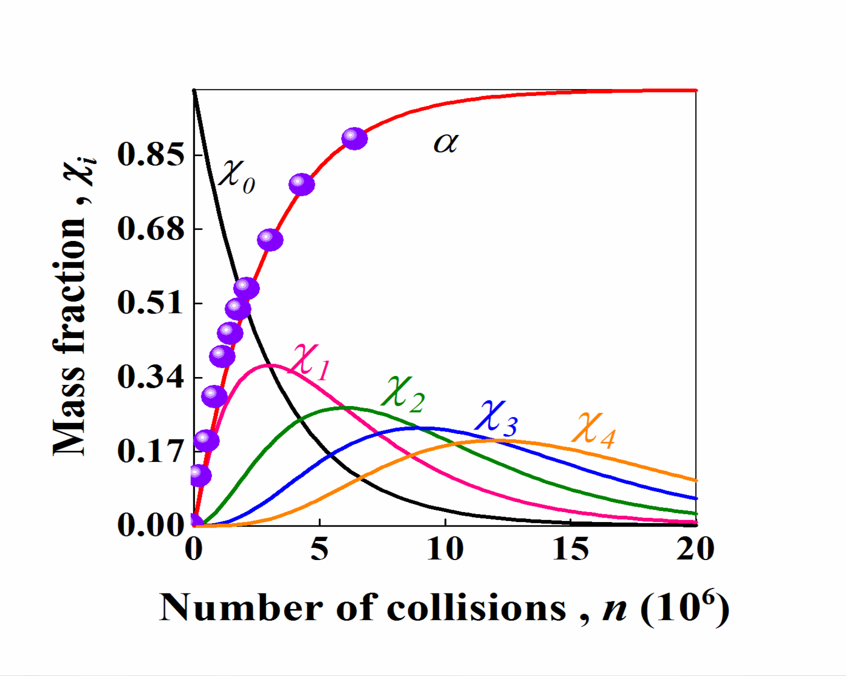

Upon 2x10^6 collisions the contribution to the amorphous fractions is due to the powders impacted for the first time

F. Delogu,, G. Cocco, Materials Science and Engineering A, 2003, A343, 314-317

Into the Microscopic scale..

- Quantification of mechanochemical parameters on absolute scale
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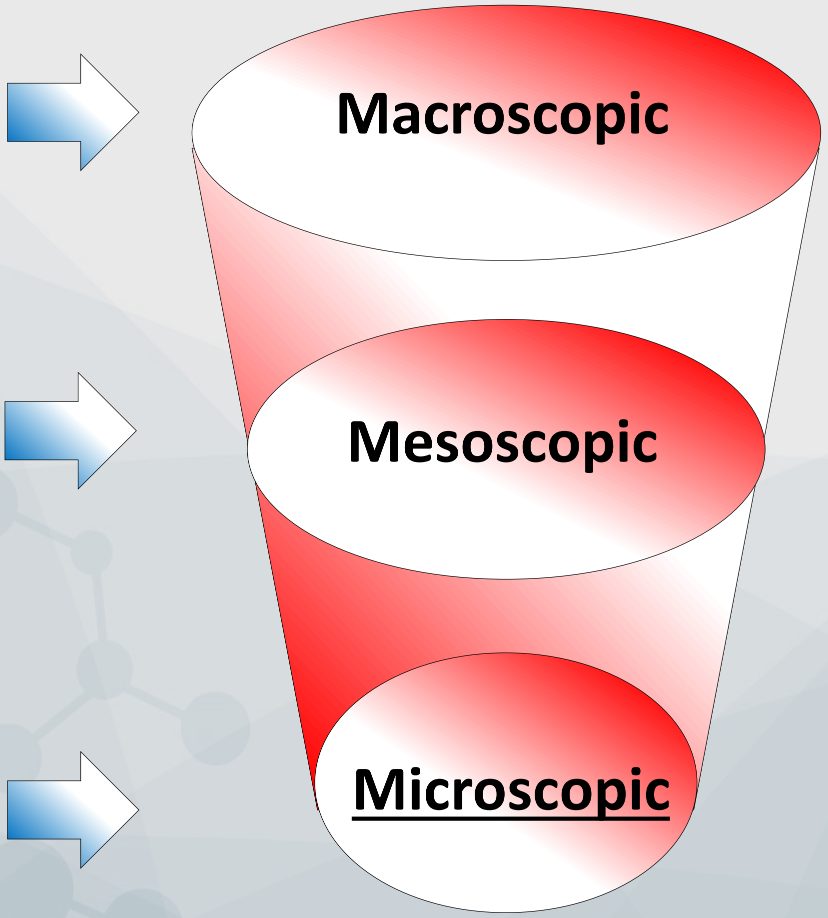


Theoretical aspects….

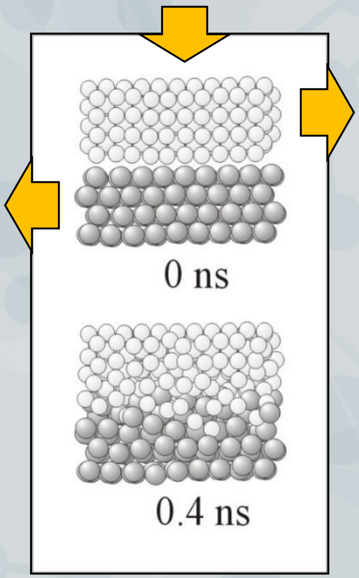
- Mechanochemical processes take place under non-equilibrium conditions, the chemical reactivity being promoted by unbalanced mechanical forces.
- Mechanical deformation occurs on a local basis, being mediated by dislocations and other lattice defects

it must be expected that the mechanical activation induces mass transport processes different from the ones operating under thermal activation conditions, with a significant impact on the physical and chemical behavior of solids at different scales.

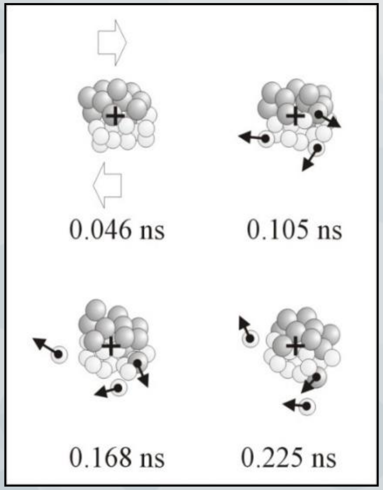
P. Balaz, et al. Chem. Soc. Rev., 2013, 42, 7571-7637

At atomic level….

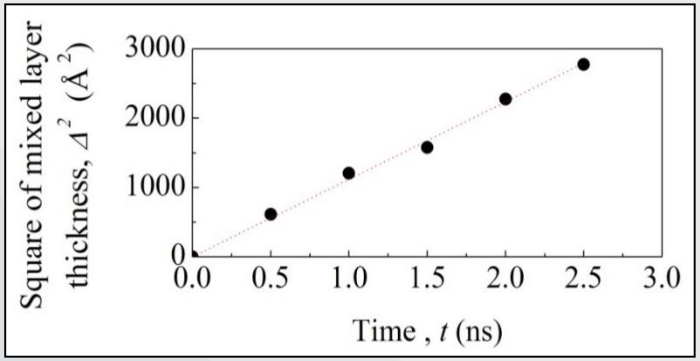
A look to the atomistic processes in metals…



Frictional sliding



Rotation of clusters



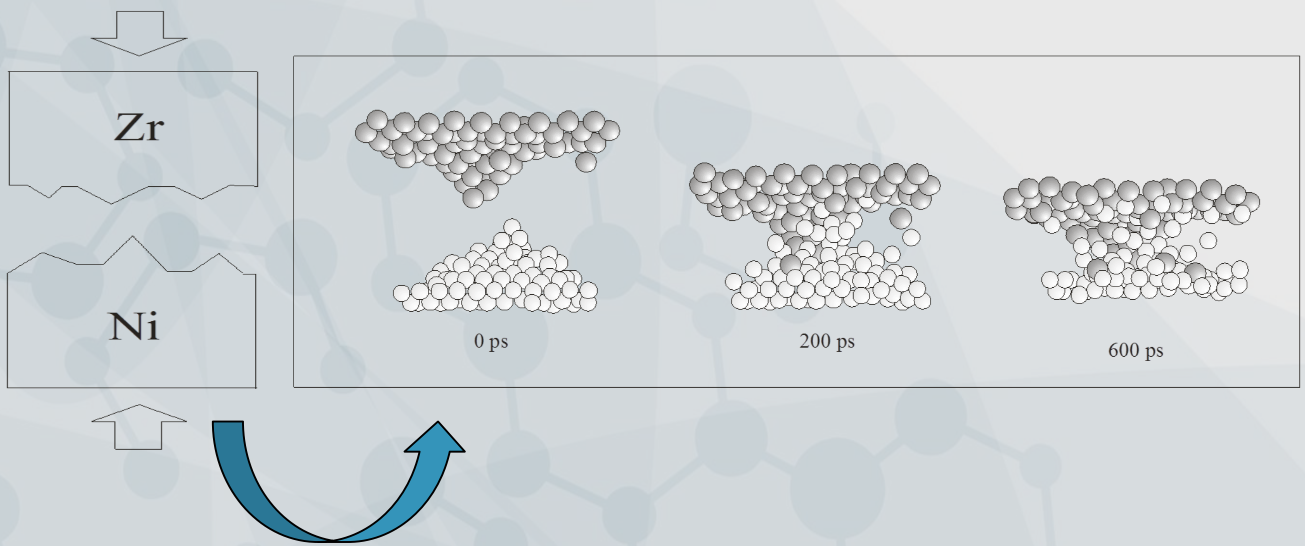
Diffusion-like dependence on time

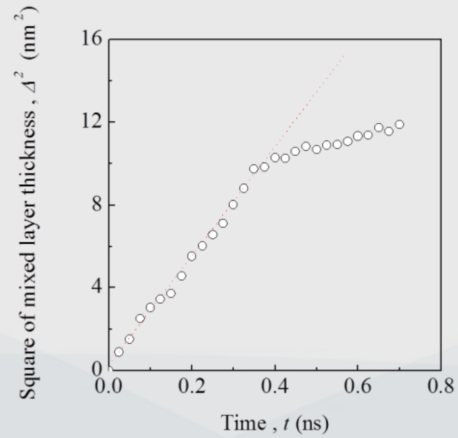
Shear-induced displacements faster than thermal ones

P. Balaz, et al. Chem. Soc. Rev., 2013, 42, 7571-7637

At atomic level….

Collision

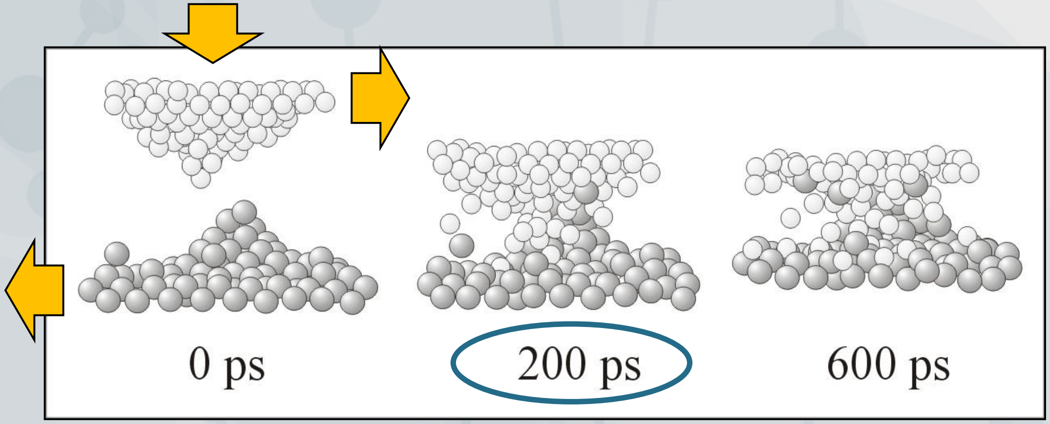




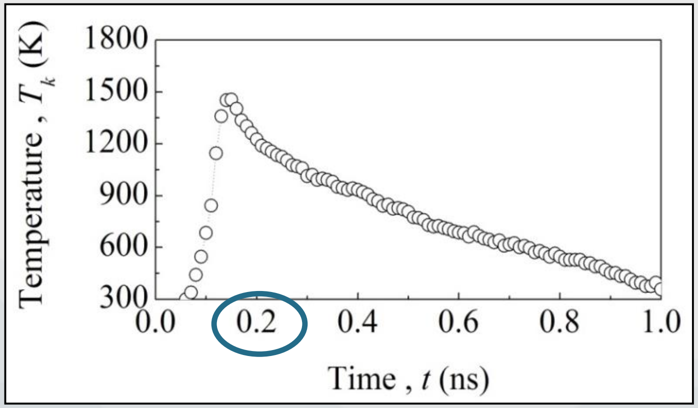
In the case of collision events, the mixing of atomic species displays two different regimes characterized by different apparent diffusion rates

At atomic level….

A look to the atomistic processes in metals…



Stress-induced mixing of* Ni *and* Zr *at a frictional collision

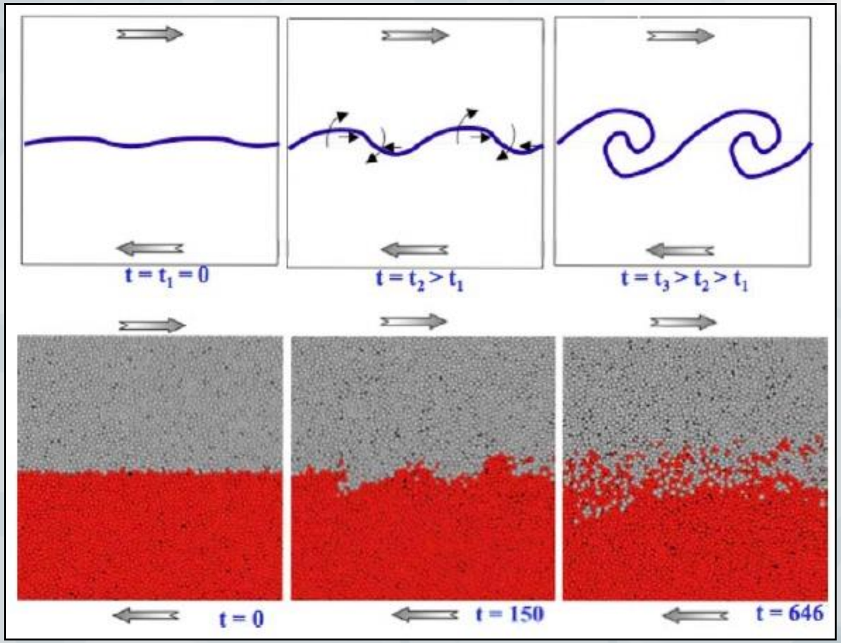


High local temperatures

The interaction of surface asperities generates liquid-like regions

Ball milling: at atomic level….

On a larger scale…

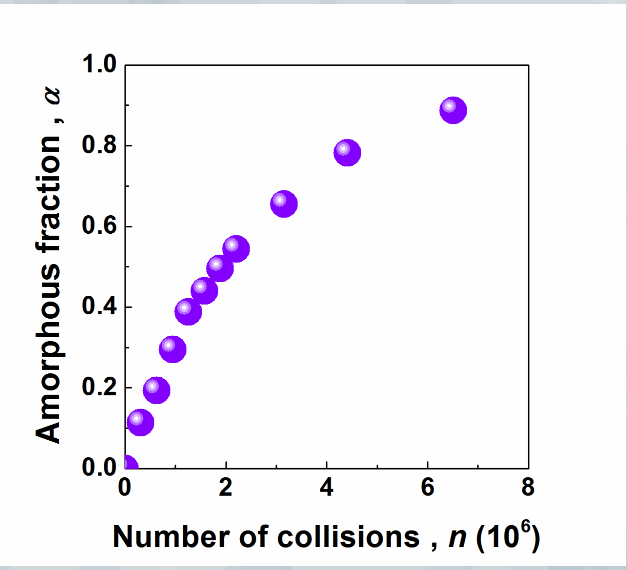


Kelvin-Helmholtz shear instabilities

Vorticity induces the refinement of the microstructure in* Cu-Fe*.

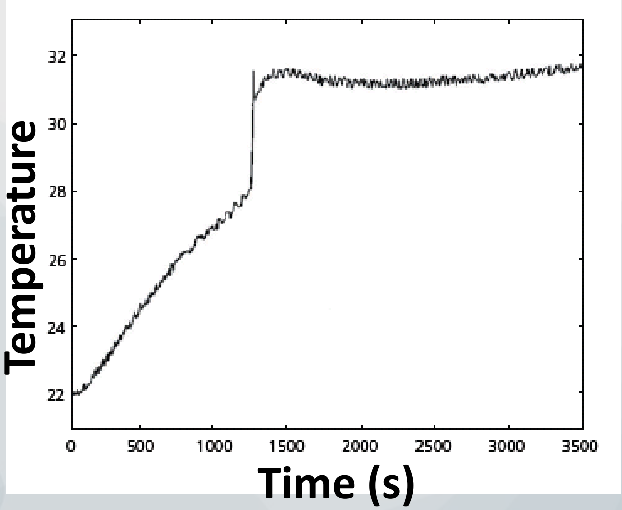
Mechanochemical reactions

Gradual



Ni-Ti
Fe-Co
Cu-Nb

Mechanically-induced self-propagating reaction (MSR)

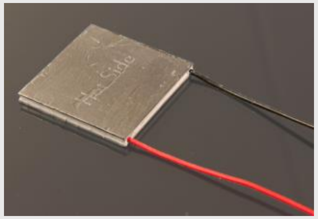


Si-C
Ti-C
$LiNH_2$-$AlCl_3$

Mechanochemical reactions

- **Bi + Te → Bi_2Te_3**

Semiconductor with a efficient thermoelectric material for refrigeration or portable power generation.



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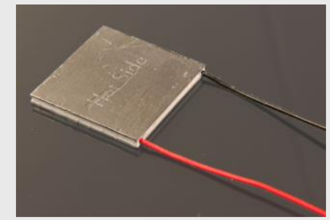


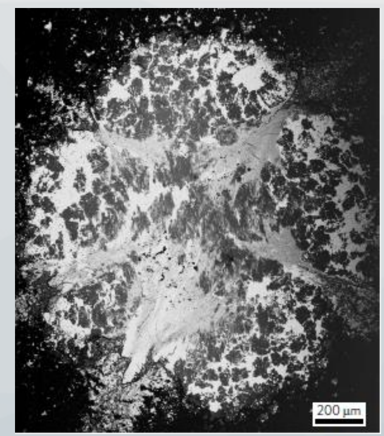
nature materials

ARTICLES

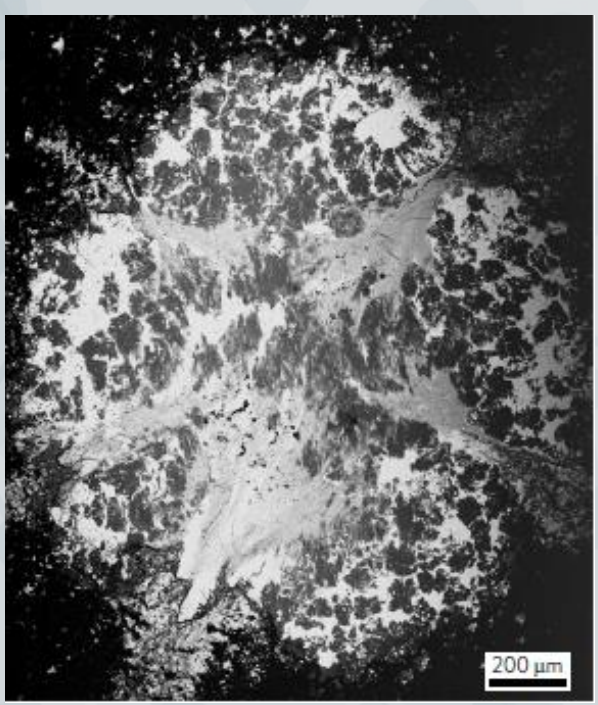
PUBLISHED ONLINE: 22 AUGUST 2016 | DOI: 10.1038/NMAT4732

Melt-driven mechanochemical phase transformations in moderately exothermic powder mixtures

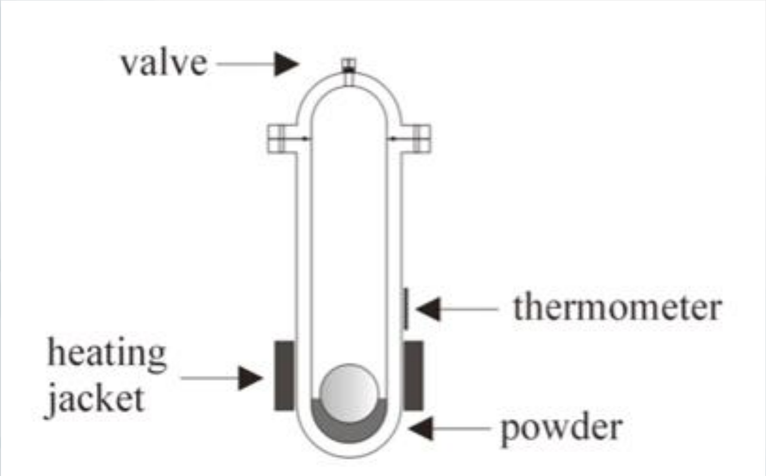
Samuel A. Humphry-Baker[1,2]*, Sebastiano Garroni[3], Francesco Delogu[4] and Christopher A. Schuh[1]



A representative collision

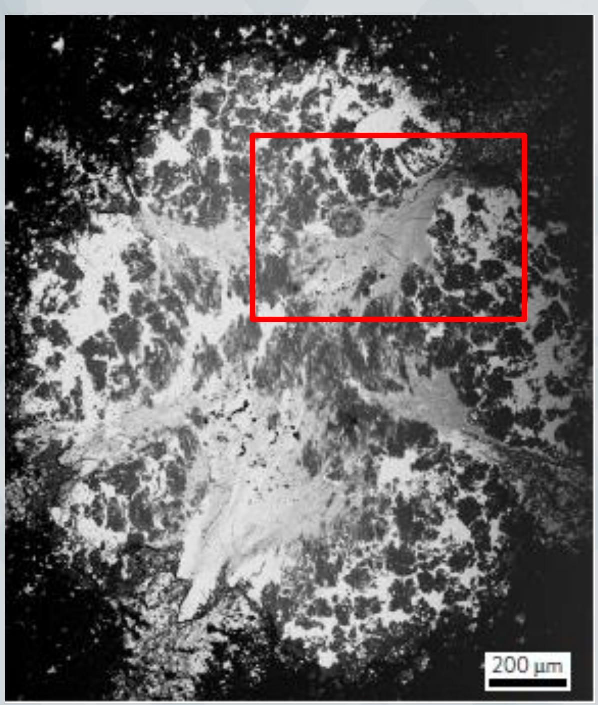


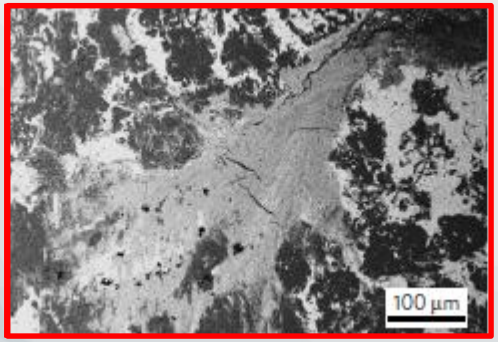
- **C**ritical **L**oading **C**ondition **(CLC)**



- S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, ***Nature Materials*** , 2016, DOI: 10.1038/NMAT4732

Typical Impact

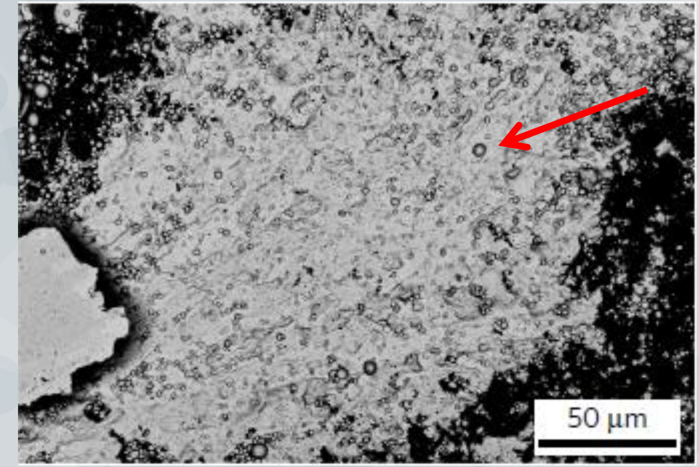




Components melted and flowed as liquid

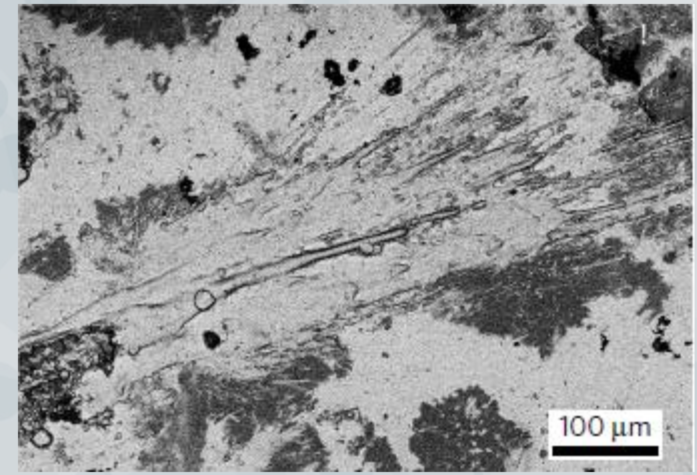
• S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, ***Nature Materials*** , 2016, DOI: 10.1038/NMAT4732

Typical Impact



- S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, ***Nature Materials*** , 2016, DOI: 10.1038/NMAT4732

Typical Impact

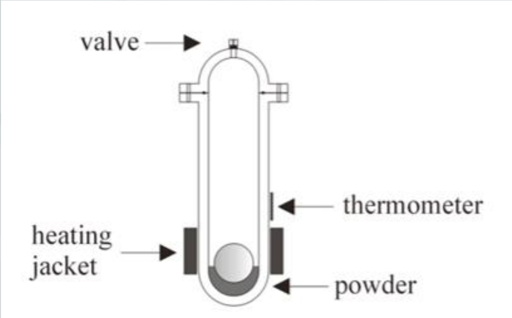


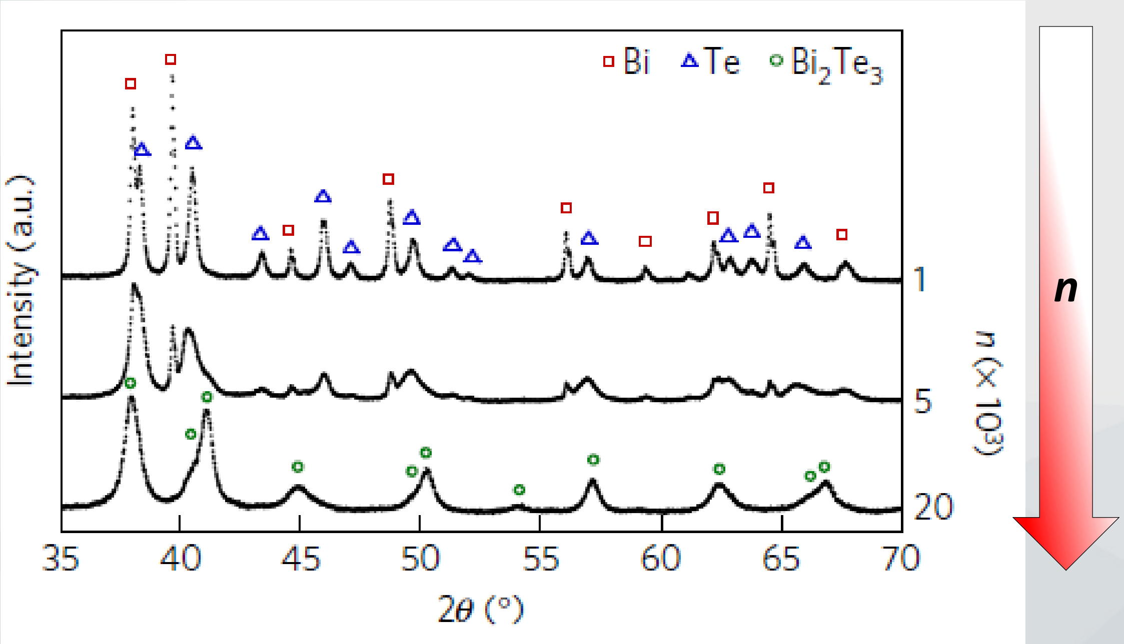
Molten Bi is formed

- **Splash marks**

- S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, ***Nature Materials***, 2016, DOI: 10.1038/NMAT4732

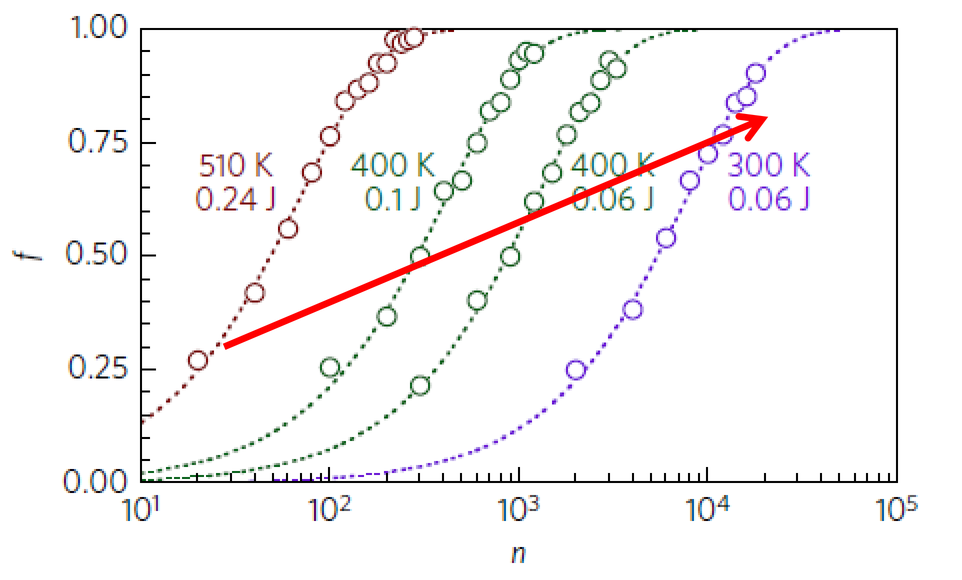
Kinetic Analysis





- S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, ***Nature Materials*** , 2016, DOI: 10.1038/NMAT4732

Fraction vs collisions

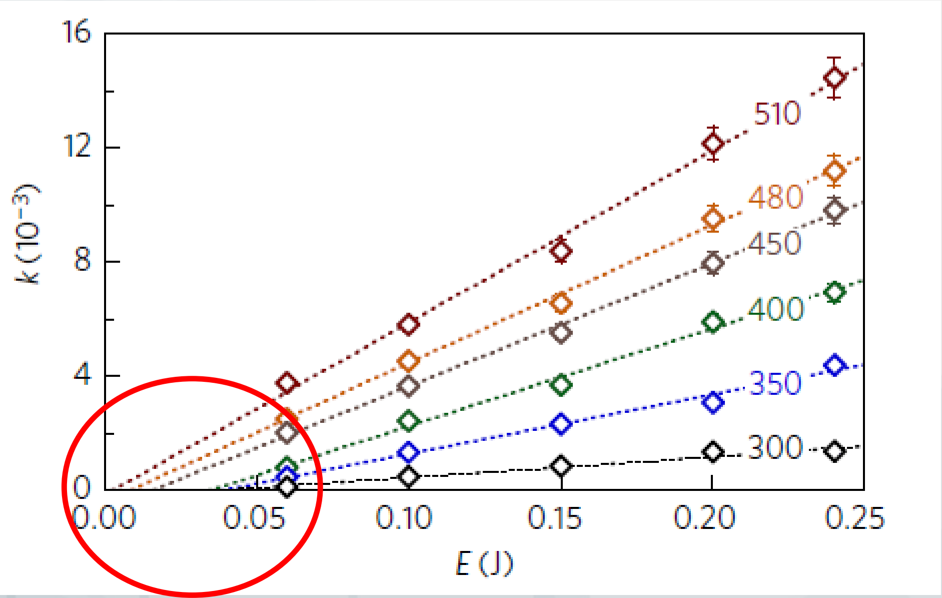


Smooth monotonic increase, but faster than gradual reaction

- S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, ***Nature Materials*** , 2016, DOI: 10.1038/NMAT4732

k vs E(J)

The rate constant, *k*, is related to the volume fraction of product



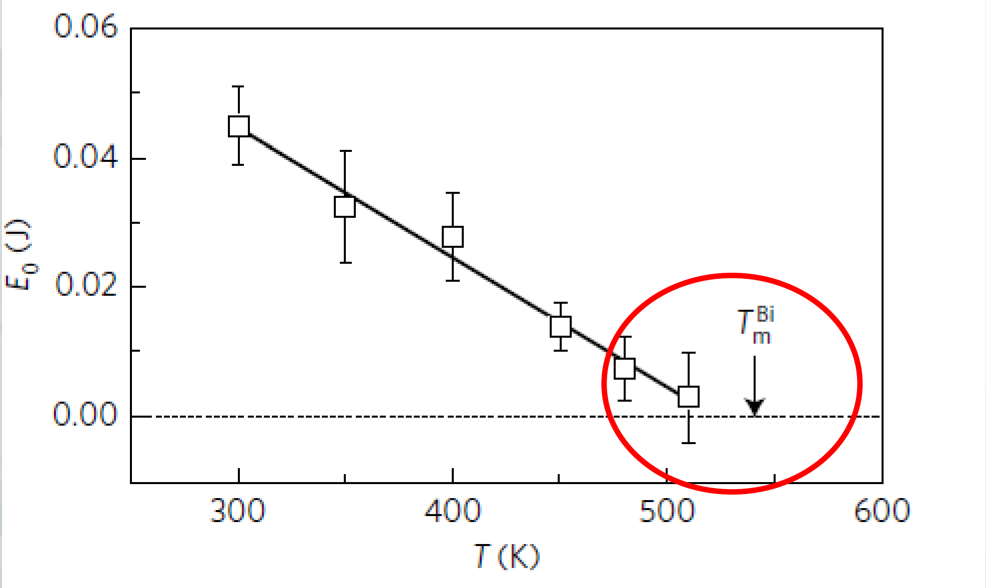
E_0 = smallest possible collision energy that give rise to any reaction

- S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, ***Nature Materials*** , 2016, DOI: 10.1038/NMAT4732

The minimum collision

ICARUS SUPERMAT

Bi T_m = 544 K

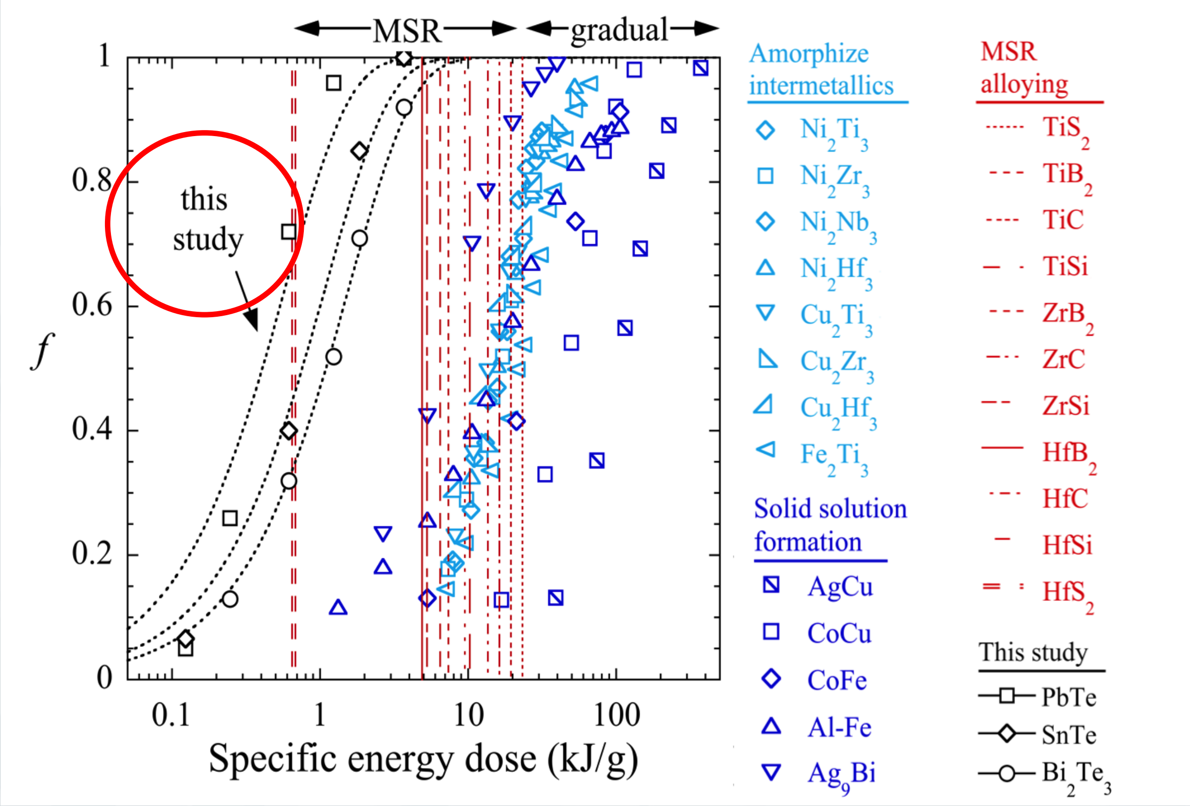


Bi melting is the kinetically controlling process of the reaction

- S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, ***Nature Materials*** , 2016, DOI: 10.1038/NMAT4732

Mechanochemical processes

New mechanochemical process has been discovered



- S.A. Humphry-Baker, S. Garroni, F. Delogu and C. Schuh, ***Nature Materials*** , 2016, DOI: 10.1038/NMAT4732

Final Remarks

- ***Organic***
- ***Organometallics***
- ***Polymers***

……..But we are in front of an unexplored territory………..

Wanderer über dem Nebelmeer

Acknowledgments

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Acknowledgments

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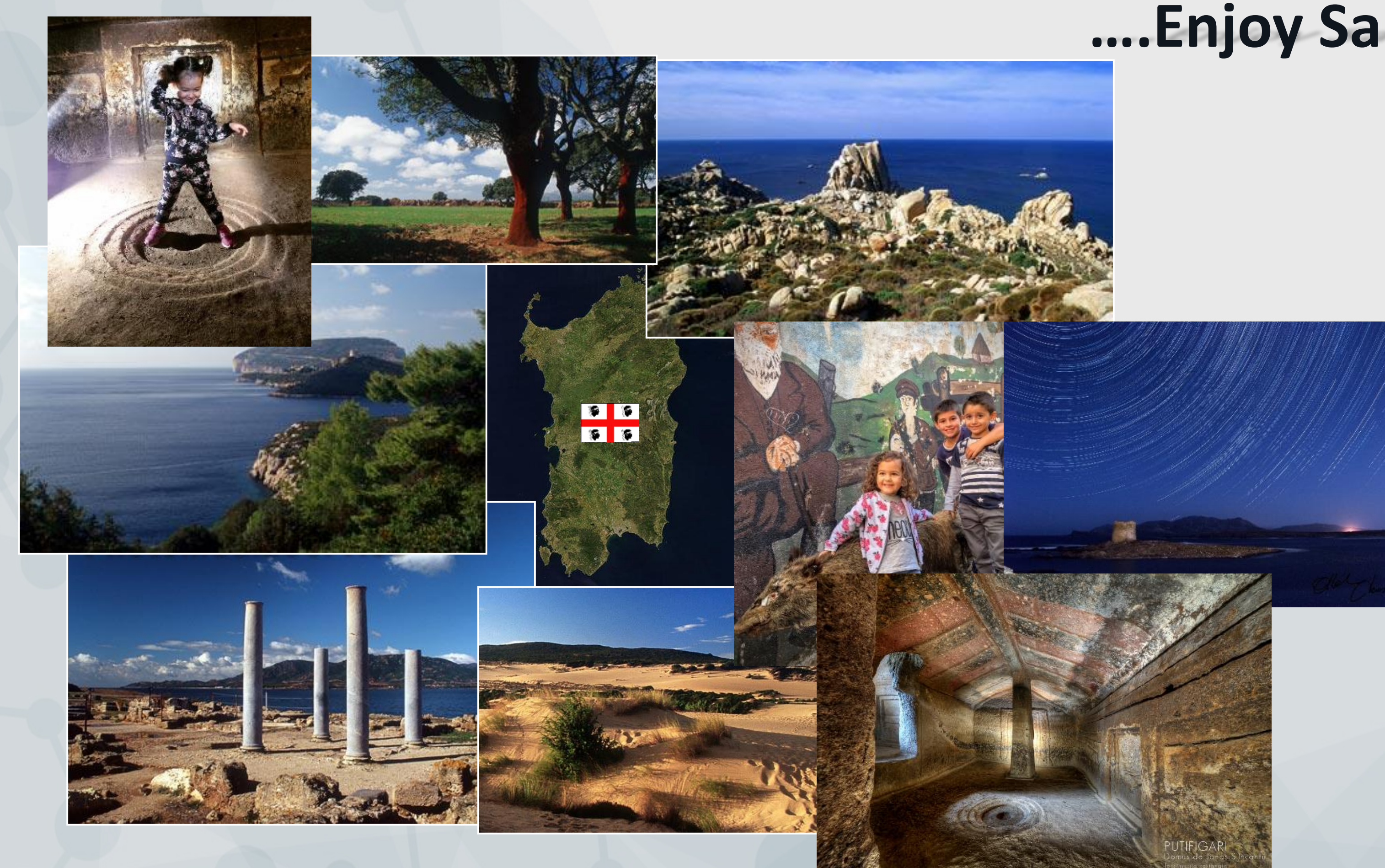
MARIE CURIE ACTIONS

NanoPiezoelectrics – Horizon2020-IF-MSCA-2015

Thank you for your attention.....

....Enjoy Sardinia



"Sardinia is out of time and history" David Herbert Lawrence, *Sea and Sardinia*, 1921

Thank you!

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Kinetic Model

after one collision the powder charge includes two volume fractions of powder processed zero and one times, and respectively. After two collisions, the volume fraction of powder processed two times, , will also appear. After *n* collisions, the volume fraction of powder that has never been subjected to CLCs can be expressed as

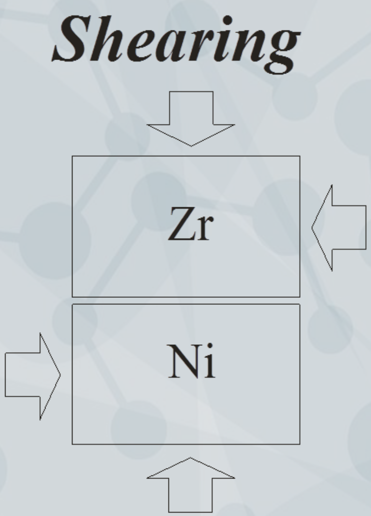
$$\chi_0(n+1) = \chi_0(n) - k\,\chi_0(n)$$

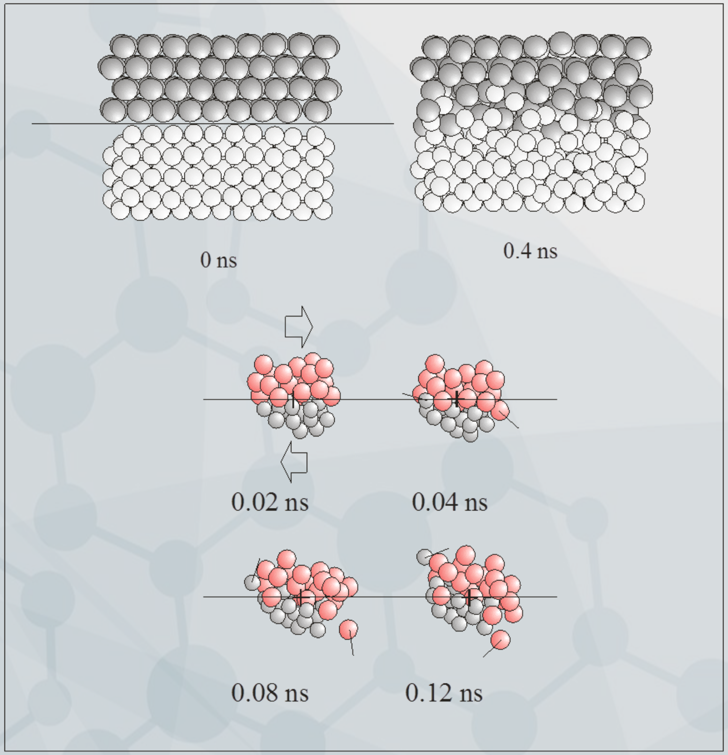
Accordingly, each collision makes decrease by the fraction . A similar expression can be written for the fraction of powder processed *i* times after *n* collisions. As shown below,

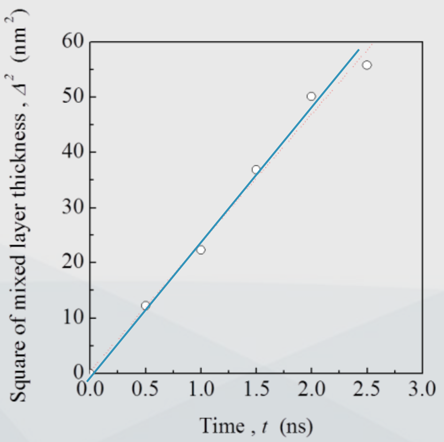
$$\chi_i(n) = \chi_i(n-1) - k\,\chi_i(n-1) + k\,\chi_{i-1}(n-1).$$

Kinetic Model

At atomic level....



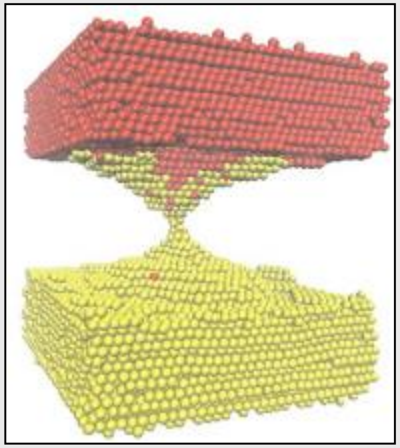


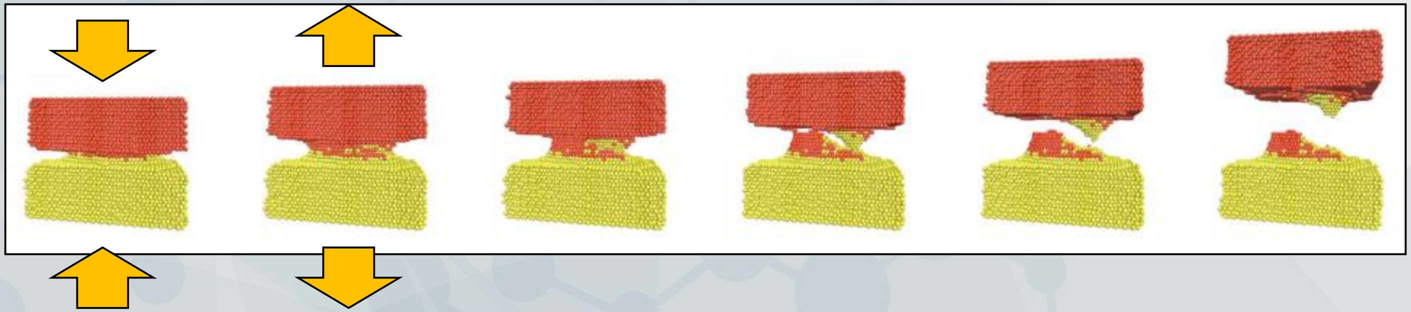


The thickness of such layer increases with time according to a power law similar to the one characteristic of thermal diffusion, although on a different time scale

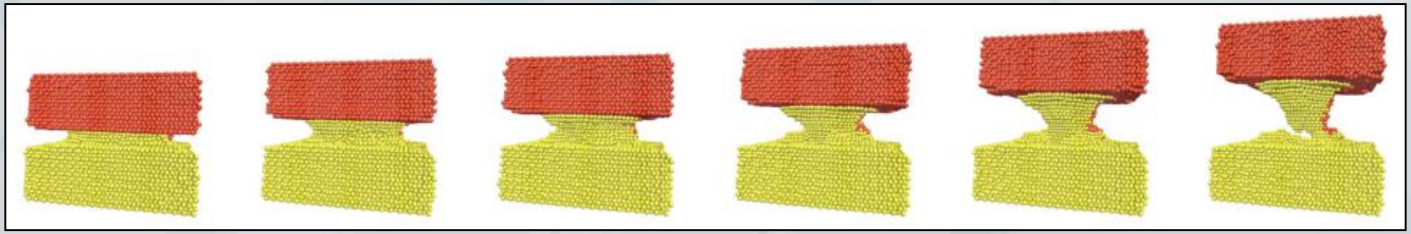
At atomic level….

A look to the atomistic processes in metals…





Role of surface asperities



Stress-induced mixing and material transfer at the Au-Ru *interface*