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ENABLING MULTI-FUNCTIONAL PERFORMANCE THROUGH MULTI-MATERIAL ADDITIVE MANUFACTURING

Assessment of occupational exposure to nanoparticles during the development of enhanced materials for metal additive manufacturing

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Nanotechnology for a better world

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- Results/Discussion
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  - Toxicology assessment
- Conclusions

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INTRODUCTION: ISQ – Company presentation

Headquarters in **Lisbon**
Founded in **1965**

SECTORS

TRANSVERSAL AREAS

International presence in 12 countries covering 4 continents

50 YEARS OF EXPERIENCE

16 ACCREDITED LABORATORIES

6 CONTACT POINTS IN PORTUGAL

MORE THAN **250** SPECIALISED SERVICES

34 AFFILIATES

1,600 EMPLOYEES

- Integrated engineering solutions
- Consultancy
- Technical inspections
- Testing
- Metrology
- Training
- **R&Di**

500 +
R&D international projects

1.200 +
partners

More information available at www.isqgroup.com

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INTRODUCTION: ISQ – Company presentation

current major roles in R&Di projects

- Risk assessment and nanosafety
- LCA/LCC
- Sustainability assessment
- Materials characterisation
- Artificial intelligence
- Development of decision support tools
- Earth observation
- Resources and eco-efficiency

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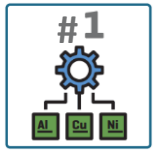
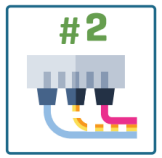
INTRODUCTION: **Multi-Fun** | Enabling MULTI-FUNctional performance through multi-material additive manufacturing

OBJECTIVES



Development of 5 new materials customized for additive manufacturing, 3 of them using nanotechnology



Development of AM equipment and software to produce the requested material compositions during the layer build-up

Manufacture and evaluate 7 physical demonstrators with multi-material design and integrated multi-functionalities: 3 use cases (structural parts, molds, test equipment) and 4 different markets (automotive, aviation, space and production industry)

Supervising the significant reduction of environmental and economic impact by Life Cycle Assessment

ISQ is participating with LCA/LCC and risk assessments/nanosafety
BCMaterials support is focused on toxicology assessment

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Which nano-enabled materials and preparation methods

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INTRODUCTION: **Nano-enabled materials**

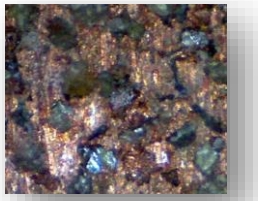
Diacool™ Metal matrix composite

Aluminum-Diamond
Copper-Diamond

Material: Diacool™ powder

Functionalisation of Diacool™ or Molybdenum powders

Copper or Chromium nano-coatings



https://www.rhp-technology.com/en

Material: Al wires (commercial)

Functionalisation of Al wires

TiC, TiB2 nanocoatings
(thickness 50-300 nm; < 150 nm)

Material: FeCrAl powder (commercial)

FeCrAl powder (~30 µm)

FeCrAl milled to obtain nanostructured material (particle size 7µm and crystallite 20nm)

Material: Al composites with TiC or TiB_2

Al powder (45 µm) + TiC nanopowders (40-60 nm) milled together

Al powder (~50 µm)

TiC / TiB_2 powder (50 nm)

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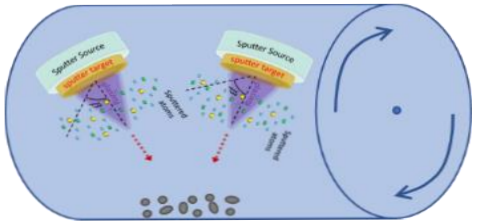
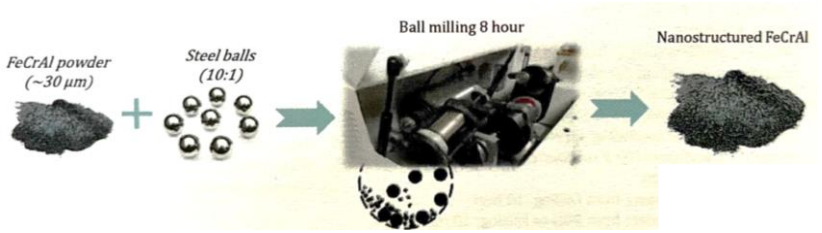
INTRODUCTION: Experimental procedures

Physical vapor deposition PVD



Ball milling



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Nanomaterials – should we be concerned

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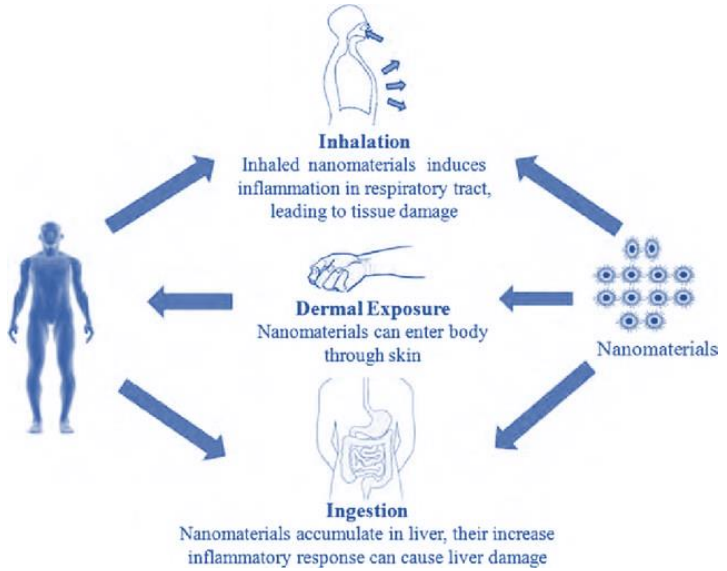
INTRODUCTION: Health and safety concerns

In comparison with the coarser similar materials, NPs are:

- Smaller
- Possess higher surface
- More reactive
- More toxic
- Remain for longer periods suspended in air
- More respirable – higher probability to deposit in the lungs
- Higher dustiness

Occupational exposure - workers can be exposed to NPs in

- Manufacturing
- Formulation
- Processing
- Transport, packaging, storage
- Cleaning and maintenance procedures
- Recycling and disposal



Ali et al. (2016). Nanomaterial Induced Immune Responses and Cytotoxicity. Journal of nanoscience and nanotechnology, 16(1), 40–57. doi: 10.1166/jnn.2016.10885

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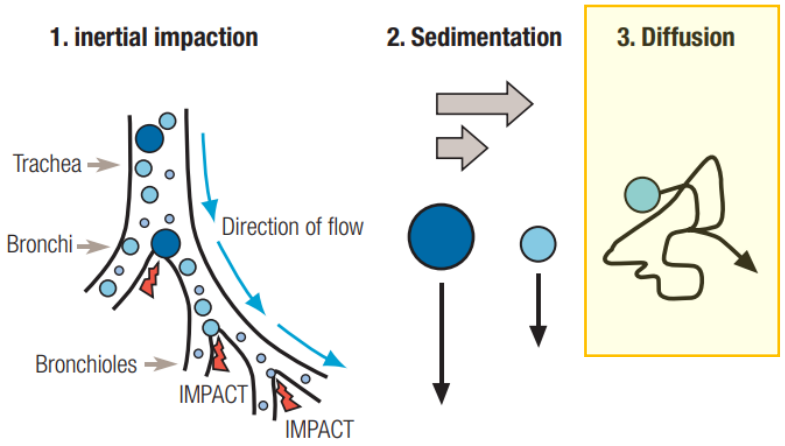
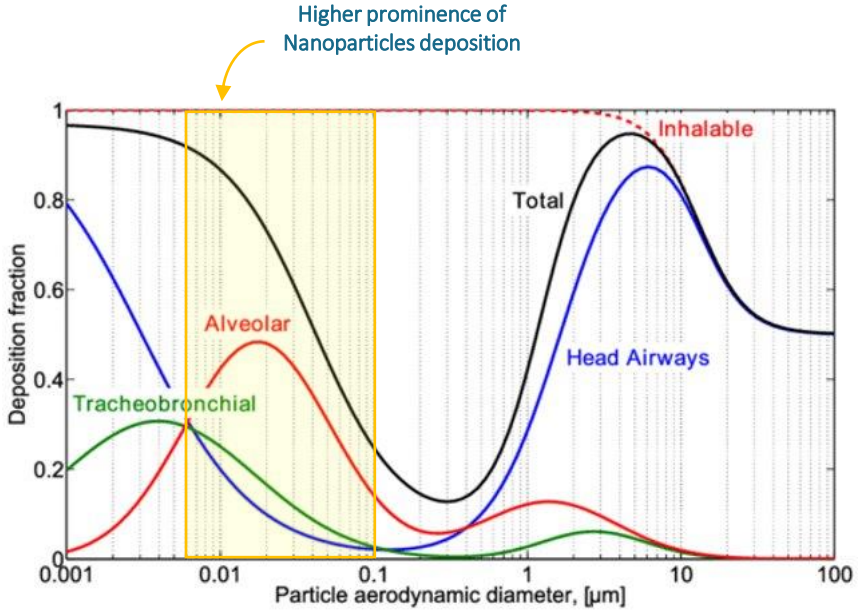
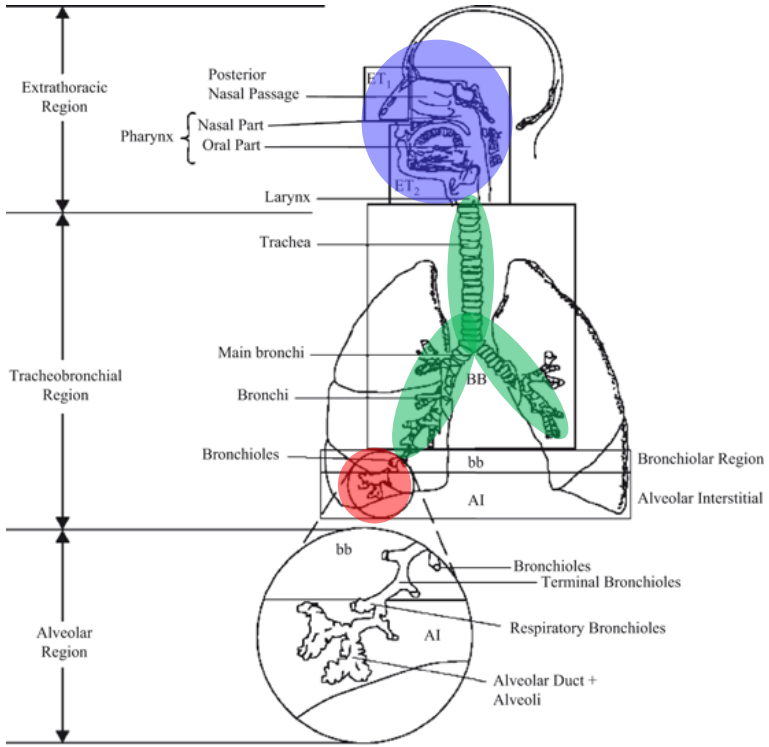
INTRODUCTION: Health and safety concerns

(Nano)particles deposition mechanisms:







Decrease in particle size means reduced efficiency of sedimentation but increased intensity of Brownian diffusion

Ka-Man Kei et al., From Aerodynamics to Inhalation Technique - More about Inhaled Medications, Hong Kong Pharmaceutical Journal, 2015, Vol. 22 (3)
Antti Koivisto, Source Specific Risk Assessment Of Indoor Aerosol Particles, Academic dissertation, University of Helsinki, 2013

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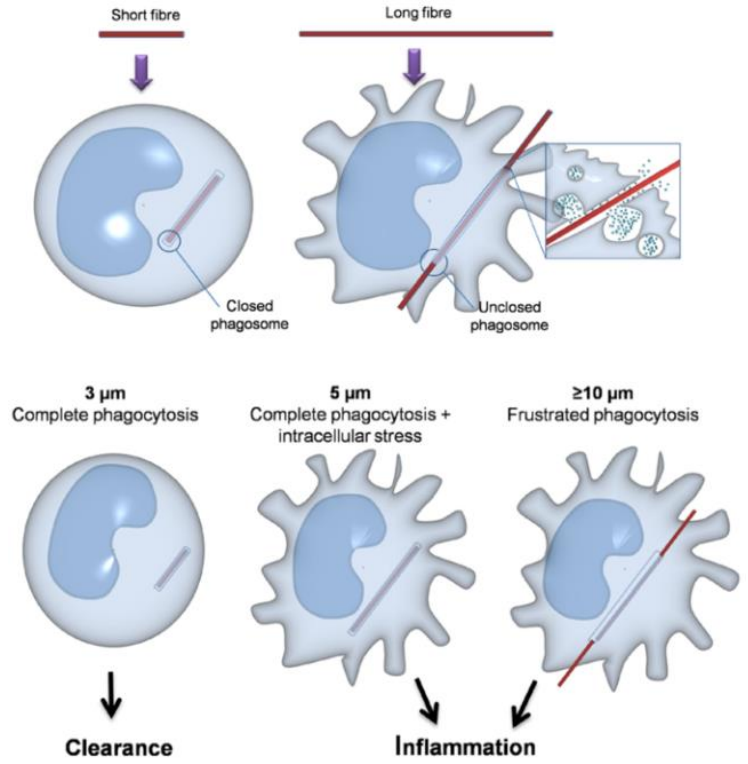
INTRODUCTION: Health and safety concerns

The **inhalation toxicity** of nanoparticles can be influenced by:

- Particle number and size
- Surface coating of NPs
- Degree of aggregation/agglomeration – aging during suspension in air (before inhalation)
- Shape/ Morphology
- Method of synthesis (wet or dry)
- Solubility
- Bio-persistency and bioaccumulation

Frustrated phagocytosis of macrophages



Schinwald, A., Donaldson, K. Use of back-scatter electron signals to visualise cell/nanowires interactions in vitro and in vivo; frustrated phagocytosis of long fibres in macrophages and compartmentalisation in mesothelial cells in vivo. Part Fibre Toxicol 9, 34 (2012). https://doi.org/10.1186/1743-8977-9-34

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What can we do to ensure safety

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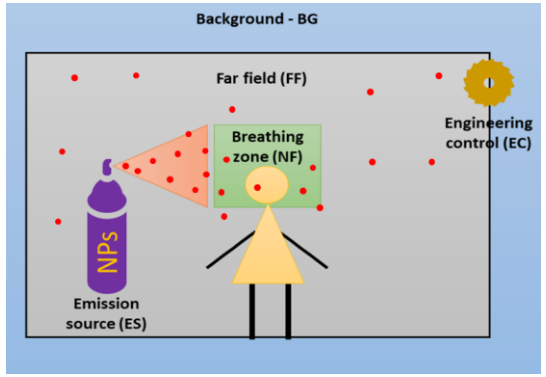
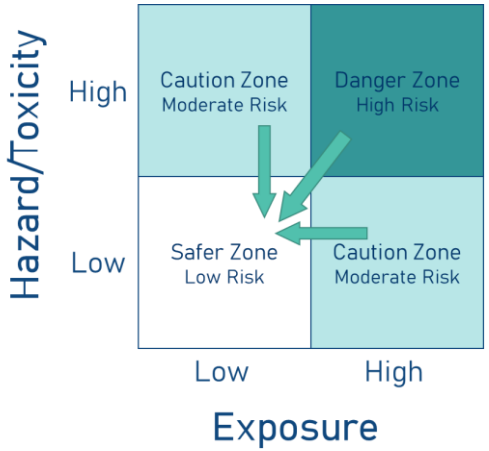
METHODOLOGY: Risk assessment

RISK = Exposure x Hazard

1. Identify the Hazards and exposure scenarios
2. Assess the exposure and characterise risk
3. Implement control measures





The main approaches to mitigate and control the risk of hazardous materials in the workplace is focused on **prevention of exposure.**

- elimination of the hazard;
- substitution of the hazard, e.g. encapsulation, use of nanoparticles in liquid media;
- engineering control techniques, e.g. glovebox, fume hoods, enclosure or isolated systems, local exhaustion ventilation;
- administrative control systems, e.g. training of people, short work shifts, work processes in shifts with less workers; clear and readable signage;
- use of personal protective equipment, e.g. face masks, gloves.

Adapted from: Gregory Morose, The 5 principles of "Design for Safer Nanotechnology", Journal of Cleaner Production, 2010, 285-289, 18(3), doi: 10.1016/j.jclepro.2009.10.001.

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METHODOLOGY: Exposure assessment

Risk screening level tools: Tiered approach

No OELs and DNELs for nanomaterials

Tier 1. Initial assessment

Information gathering

- materials
- processes
- hazards

Can the release of NPs into the workplace air be reasonably excluded?

- Identification of scenarios with potential exposure for workers
- Control Banding tools: ***Stoffenmanager Nano***

Tier 2. Basic exposure assessment

The exposure concentration is significant?
The origin is known?

- Monitoring: Particles concentration, size distribution, surface area
  - Release and background evaluation

Tier 3. Expert exposure assessment

SEM/TEM, ICP-MS

Criteria to determine if the exposure to NPs is significant

$$WA - BG > 3\sigma_{BG}$$

- Particle concentration during activity
- Particle concentration of Background
- Standard deviation

Report

A report is prepared after the monitoring campaigns providing the results of the risk assessment

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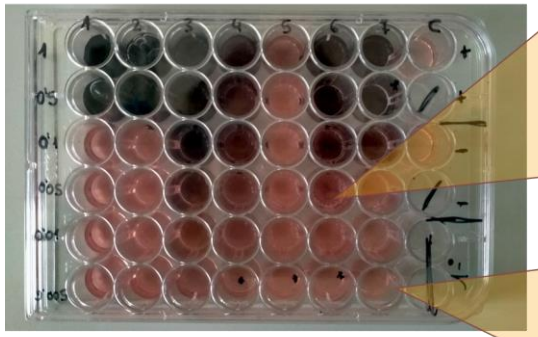
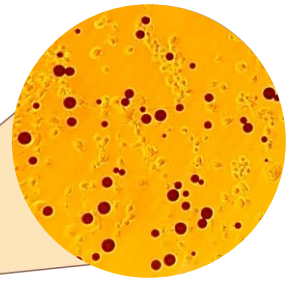
METHODOLOGY: Hazard - Toxicology assessment

Survival assessment

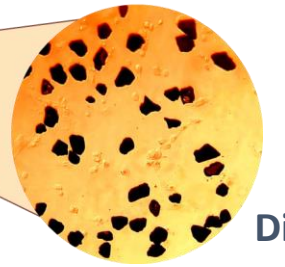
How the hazard can be assessed?

HFF1 fibroblast cells



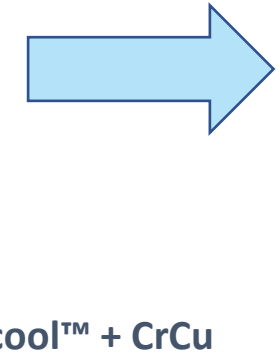


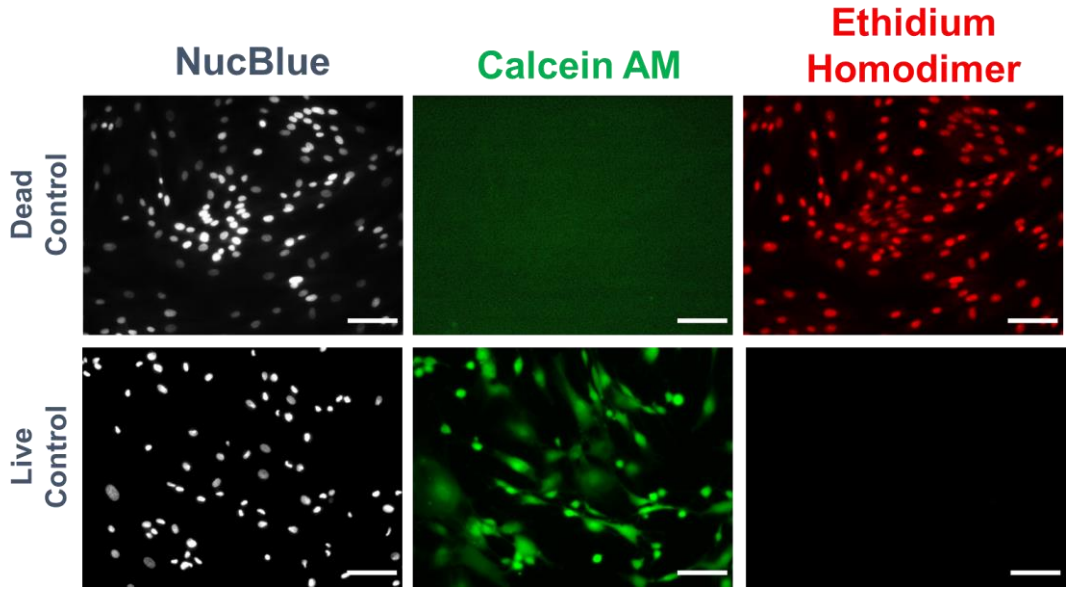
MoCu



Diacool™ + CrCu

Particles
MoCu
CCuCr
AlTiC
AlTiB2
TiB2
TiC
FeCrAl





$$m = \rho \times \frac{\Pi}{6} \times d^3 \times n$$

m - mass
ρ - density
n - particle count
d - particle diameter

RESULTS

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RESULTS: Risk screening, Control banding tool

Stoffenmanager nano

Qualitative assessment

Confirmation through monitoring by *in-situ* measurements

General data	
Product	Al TiC
Nano Particle	TiC
Concentration of the nano particle in the product	5%
Name risk assessment.	BCMaterials

Result risk assessment	**Task weighted**	**Time and frequency weighted**
Hazard class	B	B
Exposure class	1	1
Risk score	III	III

Question	**Question**
Entered data	Handling of bulk aggregated/agglomerated nanopowders
Appearance	Powder
Product dustiness	Unknown
Product moisture content	Dry product (< 5% moisture content)
Fibers	No
Fiber size.	No
Hazardous properties	Harmfull and/or irritating
Task	Handling of products in small amounts (up to 100 gram) or in situations where only low quantities of products are likely to be released.
Duration of the task	0.5 to 2 hours a day
Frequency of the task	2 to 3 days a week
Task in the breathing zone.	No
Multiple employees	Yes
Regular cleaning of the working room	Yes
Regular inspections and maintenance	Yes
Control measures at the source	Containment of the source with local exhaust ventilation
Segragation of the employee	Mechanical and or natural ventilation
Protection of the employee.	Half/full face powered air respirator TMP3 (particulate cartridge)

Risk bands matrix of Stoffenmanager Nano v1.0		Exposure band			
		1 - Low	2 - Average	3 - High	4 - Very high
Hazard band	A - Low	III	III	III	II
	B - Average	III	III	II	I
	C - High	III	II	II	I
	D - Very high	II	II	I	I
	E - Extreme	I	I	I	I

III - Low; II - Middle; I - High.

hazard class (hc)		exposure class (ec)		risk priority (risk)	
A	low	1	low	III	low
B	average	2	average	II	middle
C	high	3	high	I	high
D	very high	4	very high		
E	extreme				

Control measures already in place are included in the risk screening tool

- General ventilation
- Fume hoods
- Local exhaust ventilation

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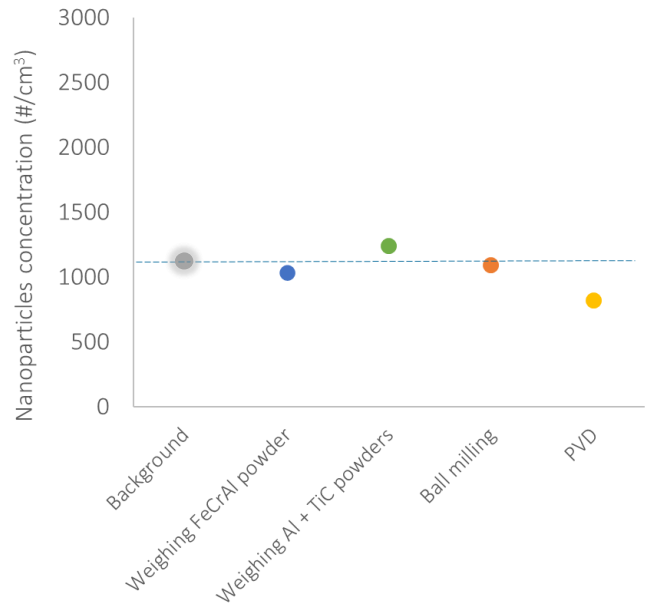
RESULTS : Exposure assessment

Monitoring of nanoparticles emission

Levels of particles in the zone of activity measured



	D_p, Mean particle size (nm)	LDSA ($\mu m^2/cm^3$)
Background	57	4
PVD	65	4
Weighing powders	57	4
Ball milling	59	3

Normal values for (low) polluted indoor environments:

LDSA = 17 $\mu m^2/cm^3$ (1)

(data obtained from NPs monitoring in 26 scenarios close to a rural location)

No significant exposure to NPs!

(1) Geiss *et al.*, Lung-deposited surface area concentration measurements in selected occupational and non-occupational environments, Journal of Aerosol Science, 96, 2016, doi: 10.1016/j.jaerosci.2016.02.007

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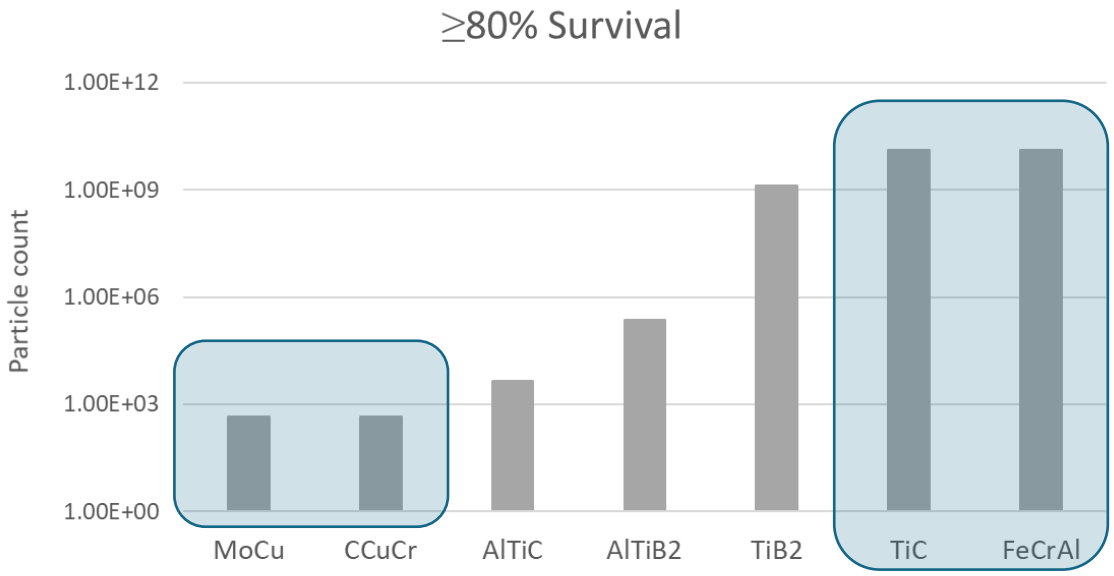
RESULTS : Toxicology assessment
CELL TOXICITY: SUMMARY



Cytotoxicity	Particles
1	MoCu
2	CCuCr
3	AlTiC
4	AlTiB2
5	TiB2
6	TiC
7	FeCrAl

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CONCLUSIONS

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CONCLUSIONS

- The Risk assessment, supported by the Tiered approach, was carried out during the preparation of nano-enabled materials for MULTI-FUN project and the preliminary qualitative risk assessment determined a low risk of exposure
- Exposure assessment – the monitoring of particles in the workplace environment confirmed the presence of NPs at low concentrations
- No significant exposure to NPs was observed
- TiC and FeCrAl were found to be the least cytotoxic particles, while the microparticles with nanocoatings are the most cytotoxic
- The surface treatment in the nanoscale applied to the powders might contribute to increase the toxicity
- The control measures already implemented are efficient to control the exposure during the preparation methods of the nanomaterials in MULTI-FUN

Safety is ensured!

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Take home message

Design and development of new nanomaterials

Safety and regulation

"Not all nanomaterials necessarily have a toxic effect, however, and a case-by-case approach is necessary while ongoing research continues"

EU-OSHA

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thank You!

For your attention

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Assessment of occupational exposure to nanoparticles during the development of enhanced materials for metal additive manufacturing

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