Up-scaling green synthesis and processing of advanced materials: opportunities for knowledge transfer toward innovative SMEs

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PRESENTATION CONTENT

1. General presentation of IMNR

2. Research directions and approach

3.Green chemistry synthesis: hydrothermal/solvothermal chemistry

4. EB-PVD coating technology

5. Additive Manufacturing & regenerative medicine

1. General presentation of IMNR

NATIONAL RESEARCH AND DEVELOPMENT INSTITUTE FOR NON-FERROUS AND RARE METALS – IMNR

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WHO WE ARE

BACKGROUND

01 July 1966
IMNR is established from:
- ICEM research team
- ICECHIM research team
- IPRAN design team

1990-2004
IMNR S.A. is a state-owned company

24 December 2004
IMNR becomes National R&D Institute

GENERAL ACTIVITY (1966-2004)

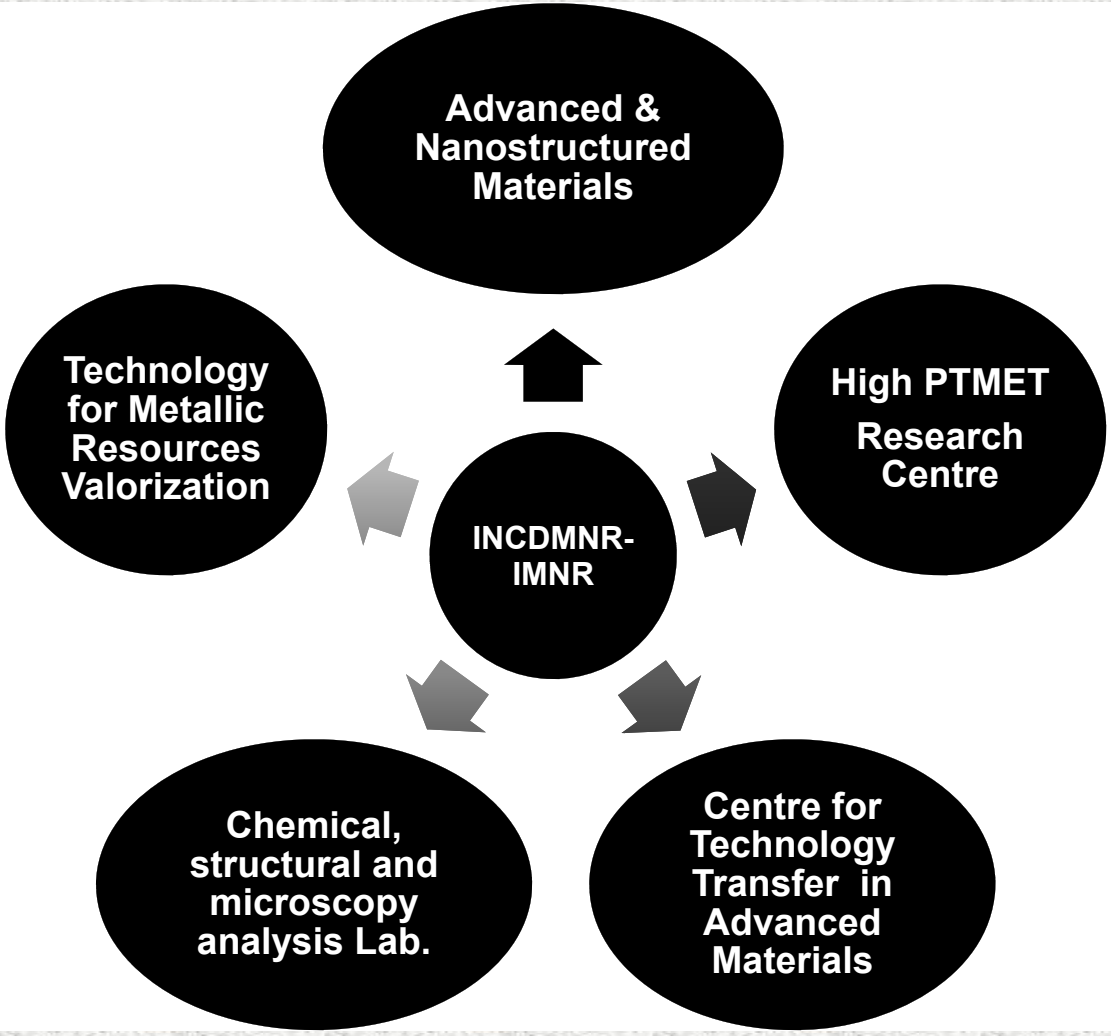
RESEARCH
- technologies for obtaining metals from Romanian primary resources:
  Cu, Zn–Pb, Al, TR, Mg, Li
- technologies for secondary resources reuse:
  In, Bi, Cd, Au, Ag, Sb, Se, Mo, W
- **Actually: emerging technologies for new materials in: aeronautics, chemistry, medicine, energy and machine building**

DESIGN
- technological installations for the recovery of: Cd, Se, In, Au, Ag, Sb
- application of licenses: Outokumpu (Cu), ISP (Zn-Pb), Pechiney (Al), Kowa Seiko (pyrite ashes)

ZIROM Giurgiu Factory

SMALL SCALE MANUFACTURE
- non-ferrous alloys
- custom made products: EB-PVD coatings

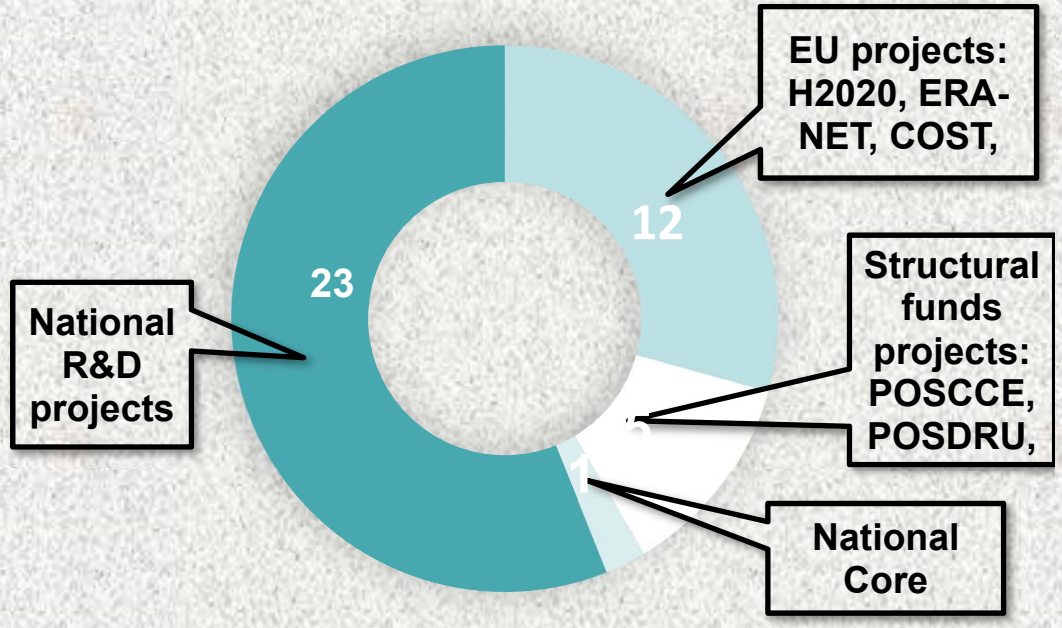
MAIN RESEARCH COMPARTMENTS



R&D PROJECTS

41 R&D PROJECTS

2013-2017



2 NATIONAL CLUSTERS

- ROHEALTH – Medicine
- MHTC Magurele – Physics & Engineering

3 EU NETWORKS (COST)

2016-2020

- HERALD: Hooking together European Research in Atomic Layer Deposition (MP14102)
- CRM EXTREME: Replacement of Critical Raw Materials for Extreme Environmental Conditions (CA15012)
- BIONECA: Biomaterials and Advanced Physical Techniques for Regenerative Cardiology and Neurology (CA16122)

4 EU PLATFORMS

- ETP Raw Materials
- EIP Raw Nanovalue
- ETP Nanomedicine
- JTI Nanofutures

NANOSTRUCTURED MATERIALS RESEARCH

EXPERTISE

- **nano-bio-materials** (ceramics, composites, hybrid inorganic-organic systems) for regenerative medicine and tissue engineering
- **thin films and advanced coatings** by hydrothermal – electrochemical processes for sensors
- **functionally graded materials** for non-conventional energy
- **new materials and functionalities** for creative manufacturing
- **thermodynamic and kinetic modelling and simulation**

EQUIPMENT

3D Bioscaffolder

drop shape analyzer

SEM Quanta 250

computer-controlled hydrothermal / electrochemical system

freeze dryer

spin coater + UV cure

high T chamber and tubular furnaces

spray-dryer

autoclave with in-situ RAMAN monitoring

DSC Maya F3 Netzsch

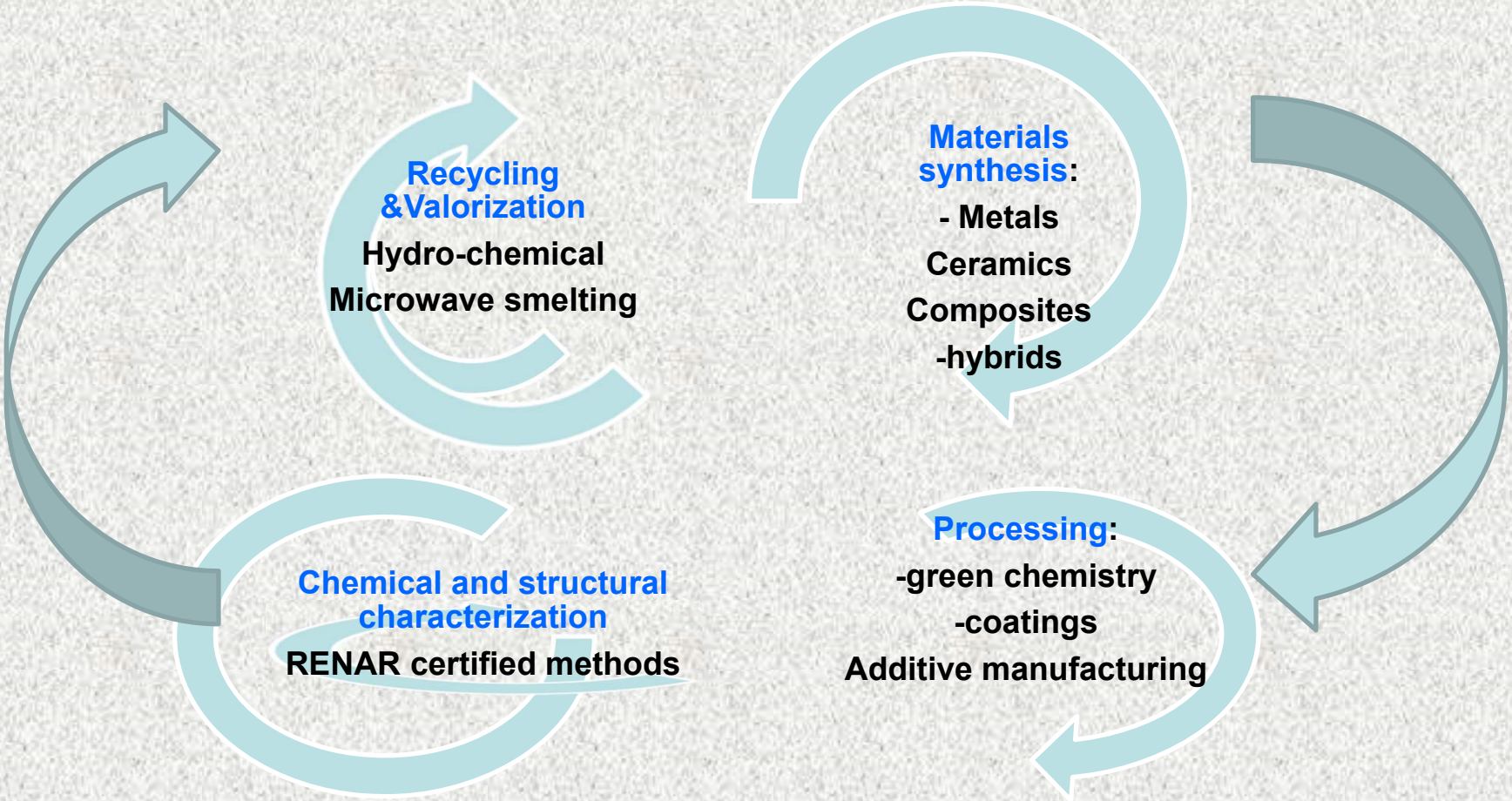
FT-IR spectrometer

Zetasizer ZS90

scratch test / AFM

Zortrax M-200

2. Research directions and approach

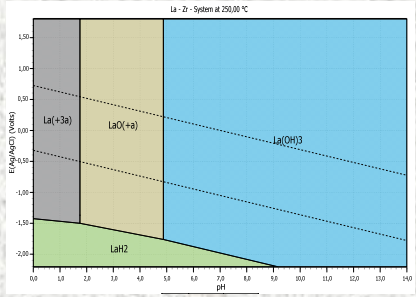


3. Green chemistry: hydrothermal/solvothermal chemistry

Laboratory & Pilot scale autoclaves
From 200 mL to 20 L
From 200 to 4000 MPa:
From RT to 250 deg. C

Main advantages:

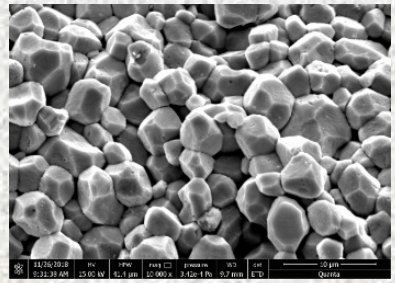
- ✓ **Closed systems, reduced environmental impact**
- ✓ **Nano-crystalline powders, no thermal treatment needed**
- ✓ **Homgeneous distribution of dopants**
- ✓ **Pressure control to low temperatures: hybrid organic-inorganic biomaterials**

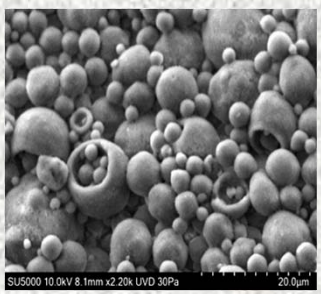


3. Green chemistry: hydrothermal/solvothermal chemistry

***Application domains-Synthesis of nanocrystalline powders*:**

- **YTZP, YSZ, doped ZrO2 for coatings and sintered products**
- **doped TiO2 for photocatalytic films**
- **Ag-ZnO – antiseptic/antifungical**
- **doped ZnO/TiO2 for superhydrophobic coatings**
- **Transition metal doped ZnO & TiO2**
- **Doped-BST: gas sensors**
- **Doped PZT: piezoelectric materials**
- **Core-shell composite powders**
- **Hybrid materials for biomedical applications: HAP – polymer for regenerative medicine – special formulated for A.M.**
- **Other nanopowders on demand**





3. Green chemistry: hydrothermal/solvothermal chemistry

Up-scaling of green chemistry processes for nanopowders synthesis

Synthesis route	**Solid state**	**Co-precipitation**	**Hydrothermal**	**Sol-gel**	**Spray pyrolysis**
Composition control	Poor	Good	Excellent	Medium	**Excellent**
Morphology control	Poor	Medium	Good	Medium	**Good**
Particle size (nm)	> 1000	> 100	10-100	>10	**>10**
Hard agglomerates	Medium	High	Low	Medium	**Low**
Impurities (%)	0.5-1	Max. 0.5	Max. 0.5	0.1-0.5	**0.1-0.5**
Additional steps	Calcinations, Milling	Calcinations, Milling	No	Calcinations, Milling	**No**
Scalability	Industrial	Industrial	Demonstration	Demonstration	**R&D**
Environmental impact	**High**	**Moderate**	**Low**	**High**	**Moderate**

4. EB-PVD coating technology

Materials in service under extreme environments:

a) metallic: refractory metals, stainless steels, high-temperature alloys

+	-
- well studied - commercially available	- corrosion problems - critical materials

b) ceramic: UHTC (ultra high temperature ceramics), oxide materials, composites.

+	-
- less corrosion - low heat transfer - replace critical materials	- less studied - structure integrity

4. EB-PVD coating technology

Oxide coatings for extreme environments

(advantages and disadvantages of these materials compared with YSZ)

Materials	Advantages	Disadvantages
Alumina	High corrosion-resistance High hardness Not oxigen-transparent	Phase transformation (1273 K) High thermal conductivity Very low thermal expansion coefficient
7-8 YSZ	High thermal expansion coefficient Low thermal conductivity High thermal shock resistance	Sintering aboce 1473 K Phase transformation (1443 K) Corrosion Oxygen-transparent
YSZ + CeO2	High thermal expansion coefficient Low thermal conductivity High thermal shock resistance High corrosion-resistance Less phase transformation between m and t than YSZ	Increased sintering rate CeO_2 precipitation (> 1373 K) CeO_2-loss during spraying

4. EB-PVD coating technology

Oxide coatings for extreme environments

(advantages and disadvantages of these materials compared with YSZ)

Materials	Advantages	Disadvantages
La2Zr2O7	Very high thermal stability Low thermal conductivity Low sintering Not oxigen-transparent	Relatively low thermal expansion coefficient
Mullite	High corrosion-resistance Low thermal conductivity Good thermal-shock resistance below 1273 K Not oxygen-transparent	Crystallization (1023-1273 K) Very low thermal expansion coefficient
Silicates	Cheap, readily available High corrosion-resistance	Decomposition into ZrO2 and SiO2 during thermal spraying Very low thermal expansion coefficient

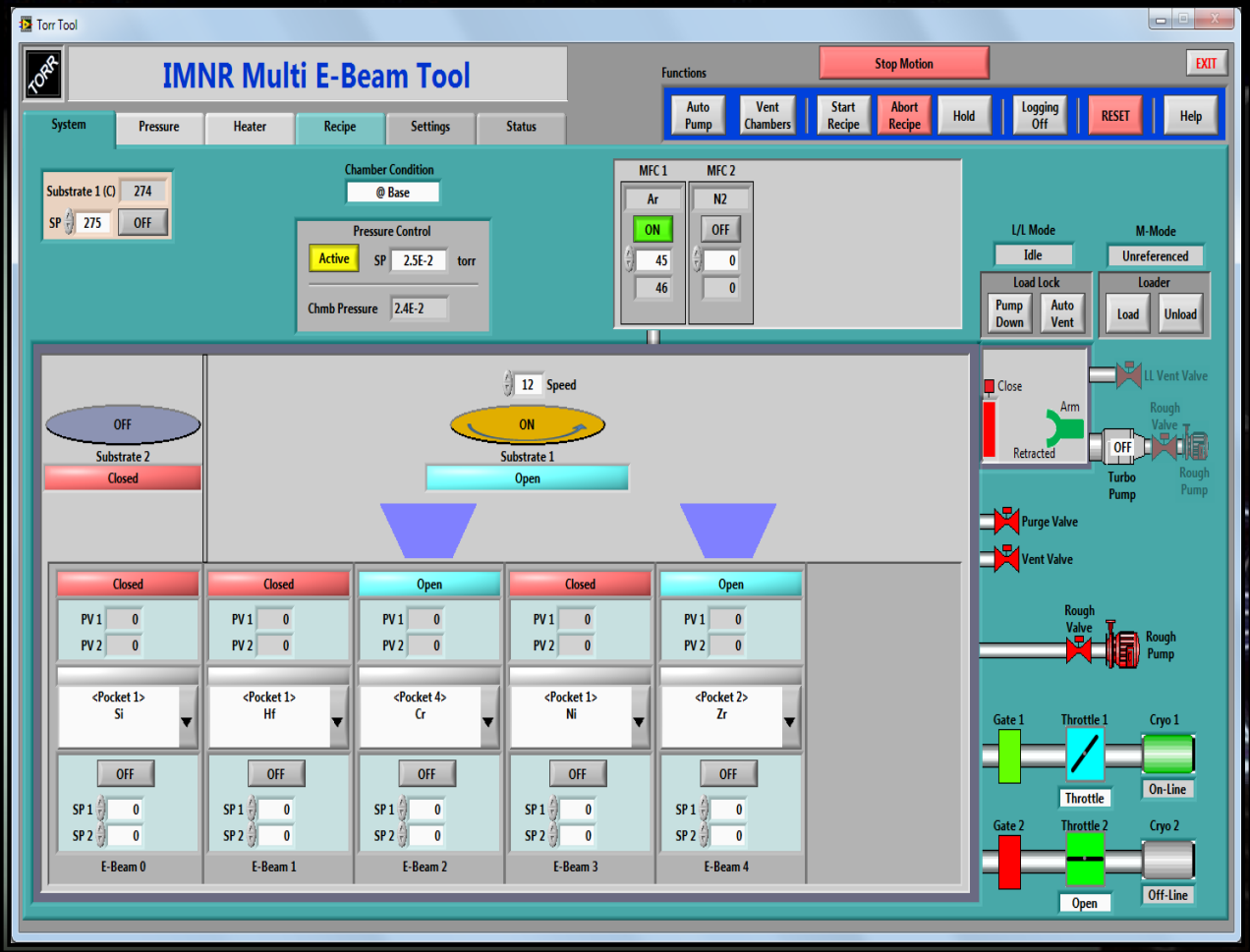
Test the limits of your mind

Today's imagination is tomorrow's innovation

- Substrate IR Heater: 16kW
- Water Cooling System: Five Closed Loop Water Chillers- 10kW
- E-Beam Power Supplies: 10kW each
- Cryo Pump Compressor: 5.5kW- Two Totaling 11kW
- Mechanical Pumps- Both Electron Beam & Thermal
- Evaporation System – 5kW
- Other ancillary components – approximately 5kW

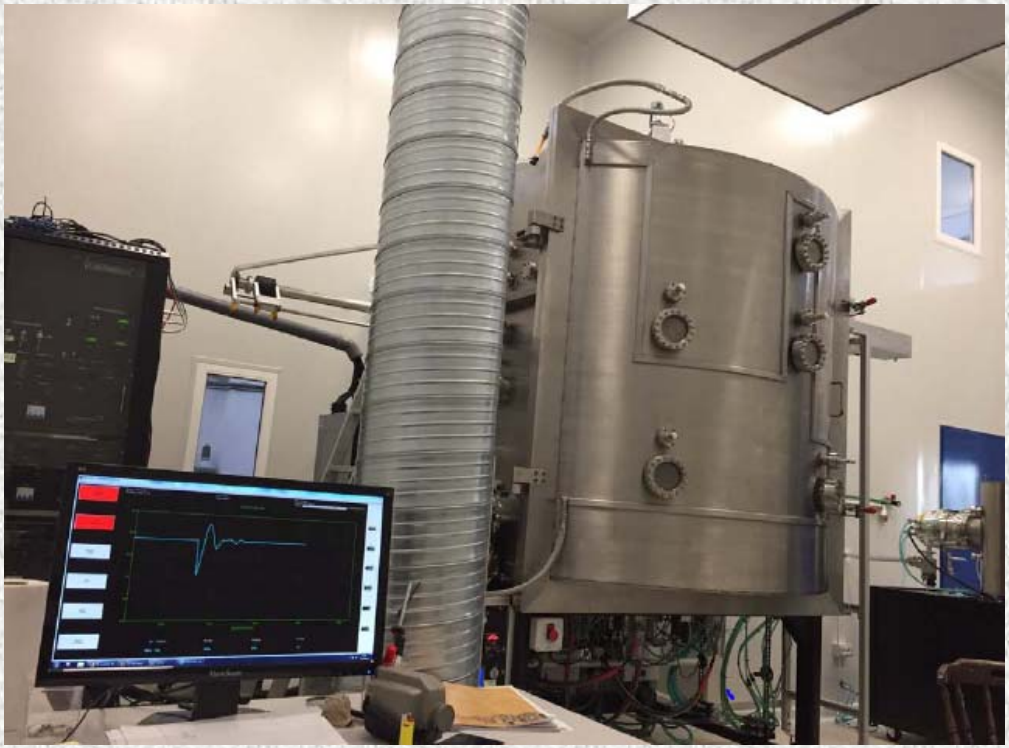
Test the limits of your mind

Today's imagination is tomorrow's innovation

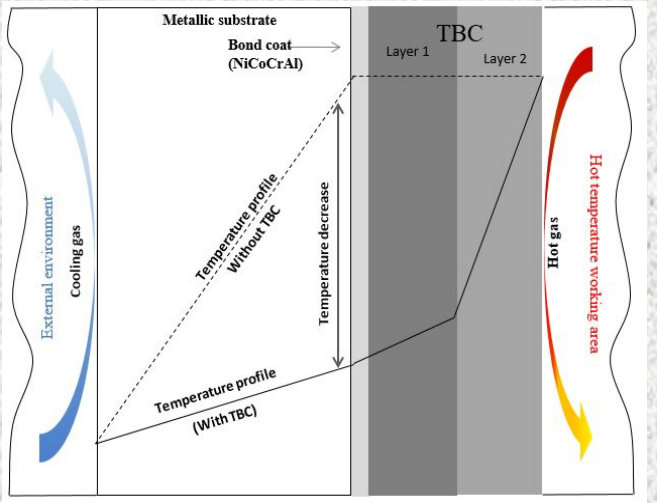


SOFTWARE LAYOUT FOR IMNR MULTI E-BEAM

4. EB-PVD coating technology

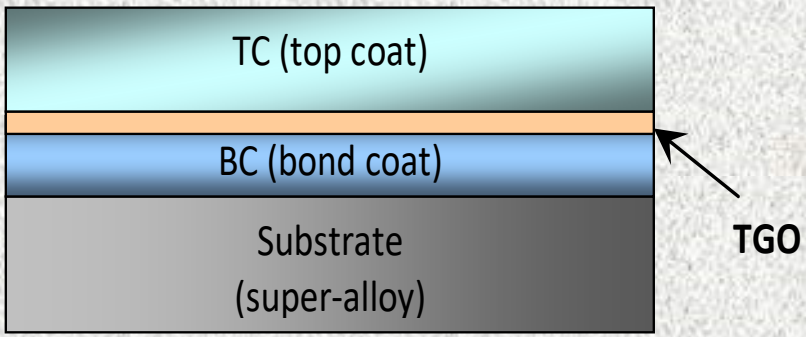


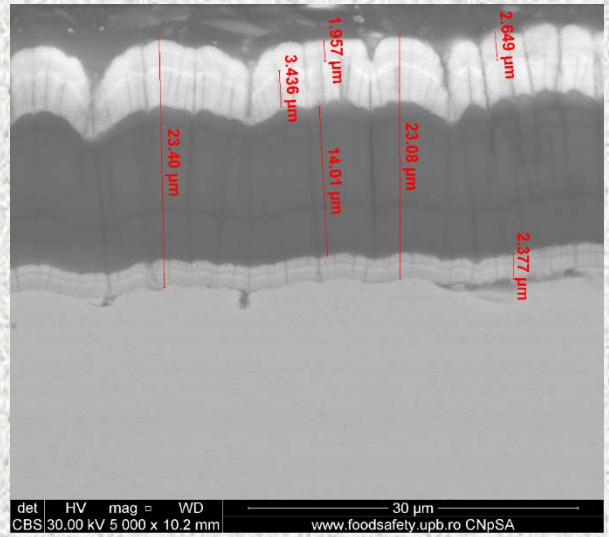
4. EB-PVD coating technology



Designed coatings arhitectures:

-Multylayer arhitectures
-Different materials
-Up to16 different materials may be deposited
-In situ controled thickness





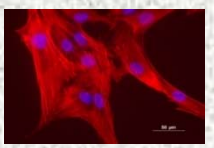
NiCrYAl/ Al2O3/REOs-doped ZrO_2/La2Zr2O7 coatings on NIMONIC 80

5. Additive manufacturing & regenerative medicine

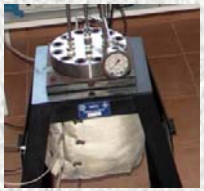
Integration of solvothermal & AM ***Processing*** ***Application***

HP Systems autoclave

Direct use



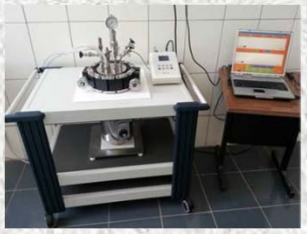
Personalized medicine



CORTEST
autoclave

equiped with

RAMAN QE Pro
spectrometer,
Ocean Optics

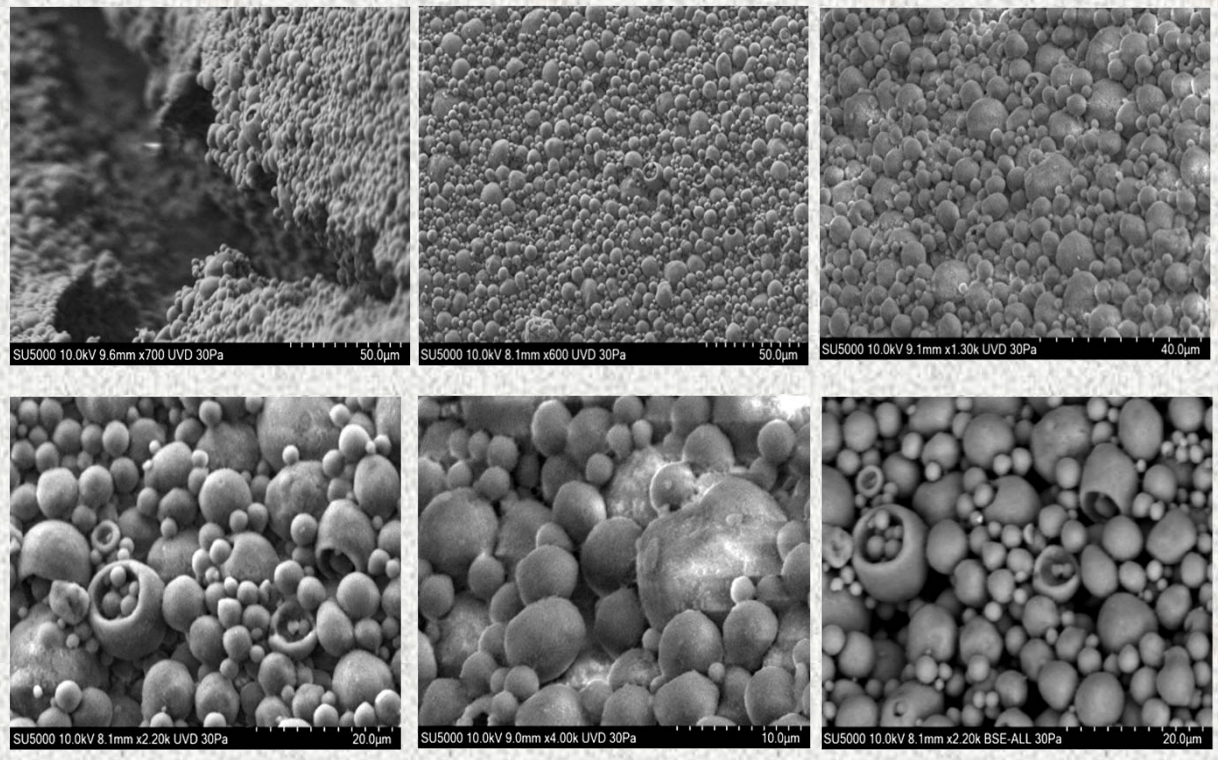


BERGHOF
autoclave

powders

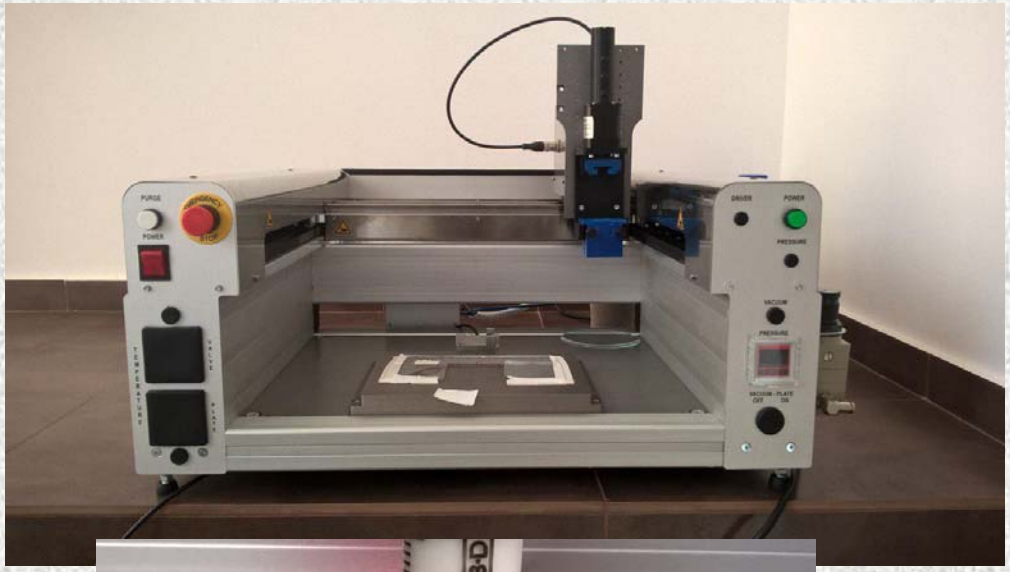
BioScaffolder

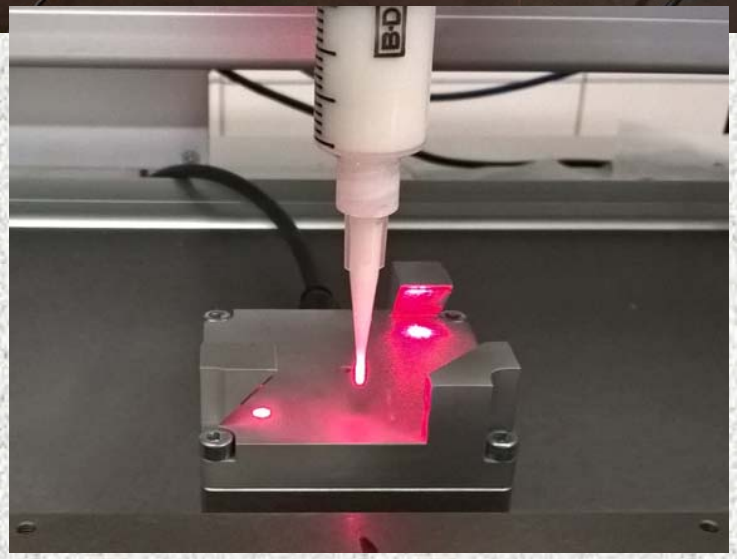
5. Additive manufacturing & regenerative medicine

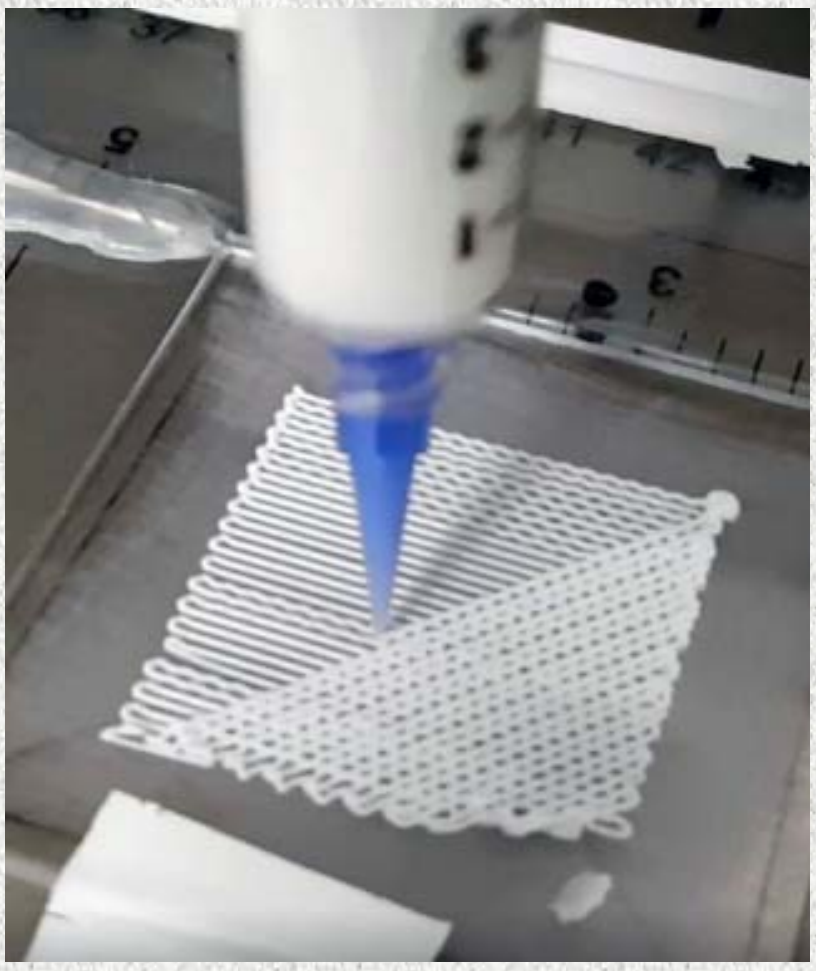


SEM pictures of a 3D sample based on Hap and commercial PU

5. Additive manufacturing & regenerative medicine







3D Bioscaffolder in use at the IMNR

5. Additive manufacturing & regenerative medicine

HYBRID MATERIALS NANOSTRUCTURED

- Multifunctional surface
- Nano-scale architecture
- Narrow polydispersity
- The terminal groups may be functionalized with chemical or biological fragments.

MARKET

- Types of material: polymers; metal; ceramics; natural (each of these presents a series of limitations)
- Medical applications requiring new materials: Cardiovascular; Dentistry; tissue engineering; Ophthalmology; Neurology; Gastroenterology; Plastic surgery; Orthopedics; Wound healing
- Applications of nanostructured hybrid materials: controlled release of drugs, contrast agents in MRI, implants, biosensors

KNOW-HOW VALUATION AND IMNR PATENT

- The possibility of customized applications
- Selection of organic functions depending on the application domain
- Technology at TRL level 4
- Validated results in national and European projects

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