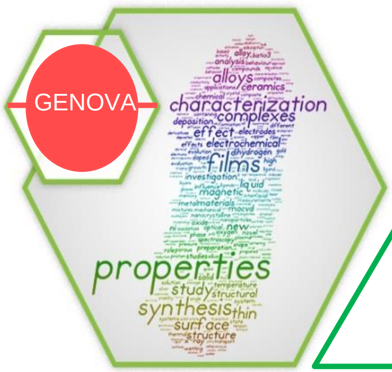
Consiglio Nazionale delle Ricerche
Istituto per l'Energetica e le Interfasi

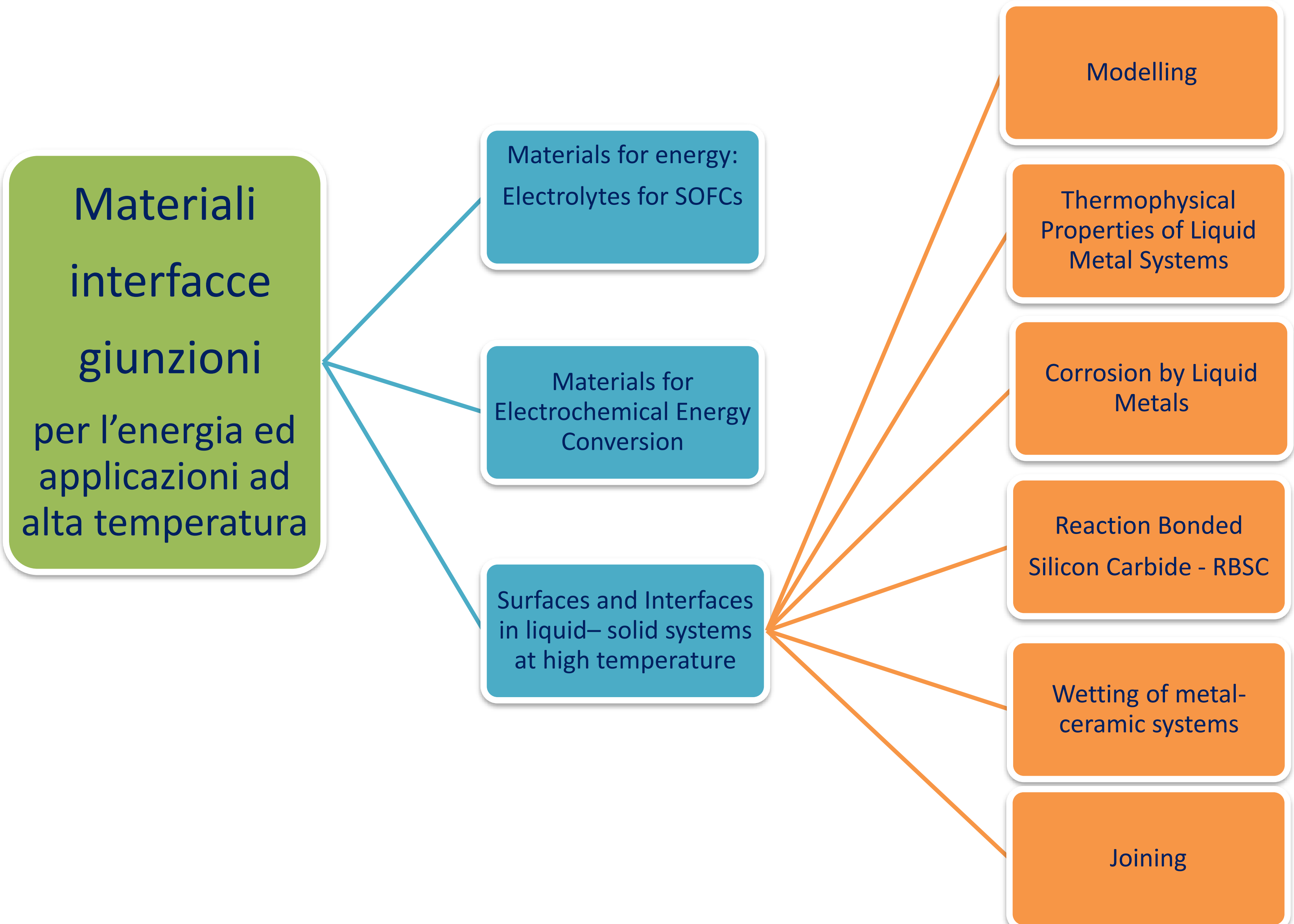
Conferenza di Istituto **Padova, 29 Febbraio – 1 Marzo 2016**



Materiali, interfacce e giunzioni per l'energia ed applicazioni ad alta temperatura

Maria Luigia Muolo

U.O.S Genova


Materiali
interfacce
giunzioni
per l’energia ed
applicazioni ad
alta temperatura
Materials for energy:
Electrolytes for SOFCs
Materials for
Electrochemical Energy
Conversion
Surfaces and Interfaces
in liquid– solid systems
at high temperature
Modelling
Thermophysical
Properties of Liquid
Metal Systems
Corrosion by Liquid
Metals
Reaction Bonded
Silicon Carbide - RBSC
Wetting of metal-
ceramic systems
Joining

Materiali
interfacce
giunzioni
per l’energia ed applicazioni ad alta temperatura

Materials for energy: Electrolytes for SOFCs

Giovanna Canu
Maria Teresa Buscaglia - Vincenzo Buscaglia

Materials for Electrochemical Energy Conversion

Surfaces and Interfaces in liquid– solid systems at high temperatures

Thermophysical

Corrosion by Liquid

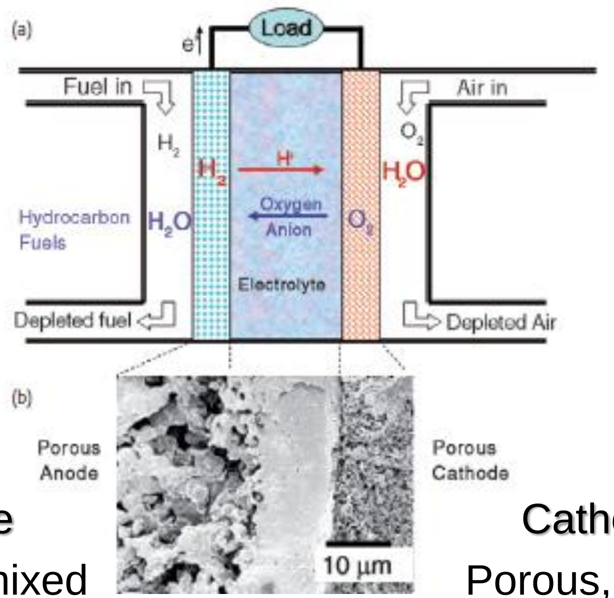
Joining

POSTER P17

Scheelite-type $LaW_xNb_{1-x}O_{4+x/2}$ electrolyte: synthesis, characterisation and chemical compatibility with electrode materials

Materials for energy: SOFCs

- Solid oxide fuel cells (SOFCs): electrochemical device which converts chemical energy into electricity, made up of all solid state materials



Anode
Porous, mixed electronic/ionic conductor

Cathode
Porous, mixed electronic/ionic conductor

Electrolyte
Core of the SOFC, dense, oxide ion- or proton-conductor

- Based on the chemical reaction between H_2 (at the anode) and O_2 (at the cathode) to produce water
- Main components:
  - Electrolyte, cathode and anode
- Other components:
  - Current collectors, Interconnects

Activities

1. Ionic conductors and mixed conductors materials
2. Electrodes for SOFCs operating at intermediate temperatures
3. New design for SOFCs

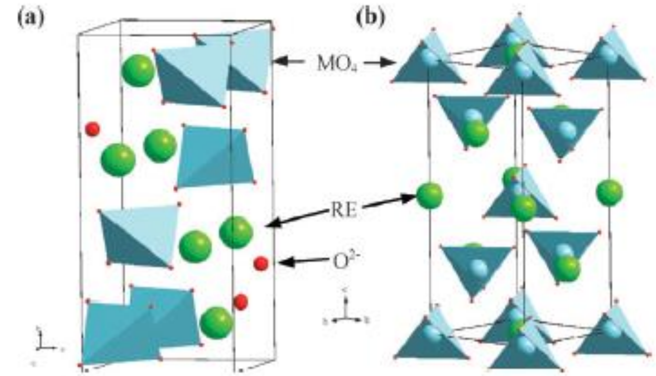
Liu at al., Materials Today 14, 11 (2011)

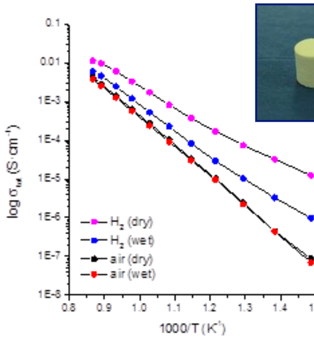
Electrolytes for SOFCs – poster P17

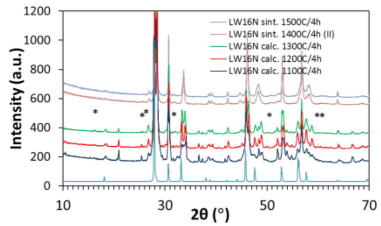
FIRB2012

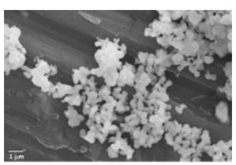
INCYPIT

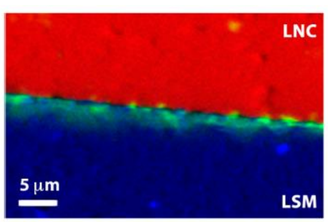
- Research on $LaNbO_4$-based materials
- Recently proposed as proton conductors (Haugsrud, Norby, *Nature Materials* 2006, 56, 193)
- High stability in CO_2-containing atmospheres and water vapour environments, unlike perovskite-based materials

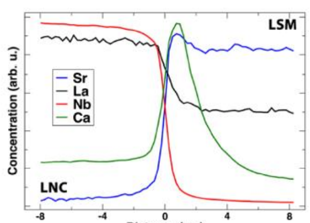












ESRF

- The activity is focused on the use of innovative approaches to overcome the limitations of the material, *e.g.* in terms of solubility of dopants, conductivity, etc.

- It is developed through the synthesis, structural, microstructural, electrochemical characterisation of materials

Materiali

interfacce

giunzioni

per l'energia ed applicazioni ad alta temperatura

Materials for Elettrochemical Energy Conversion

Massimo Viviani   Sabrina Presto

Antonio Barbucci   Paola Carpanese

Materials for Energy: Electrolites foe SOFCs

Surfaces and Interfaces in liquid– solid systems at high temperatures

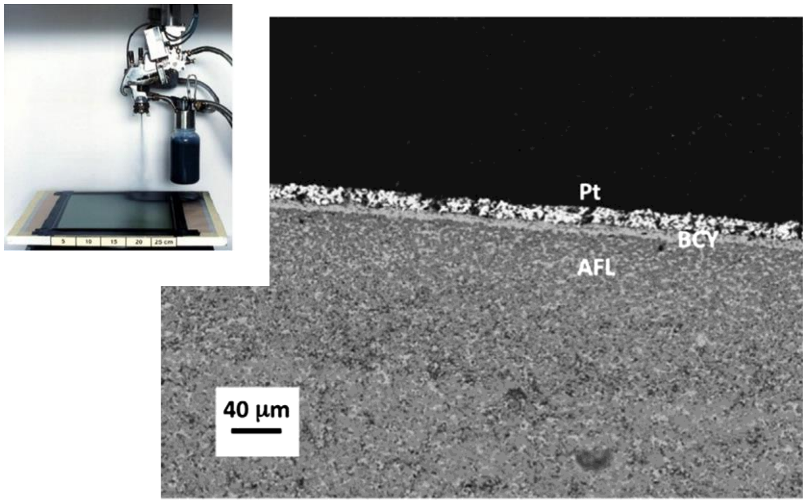
- Thermophysical
- Corrosion by Liquid
- Joining

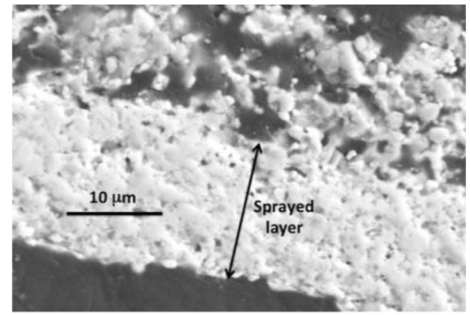
POSTER P36

MErgELab: Materials and Electrochemical processes for Energy

Materials for Electrochemical Energy Conversion

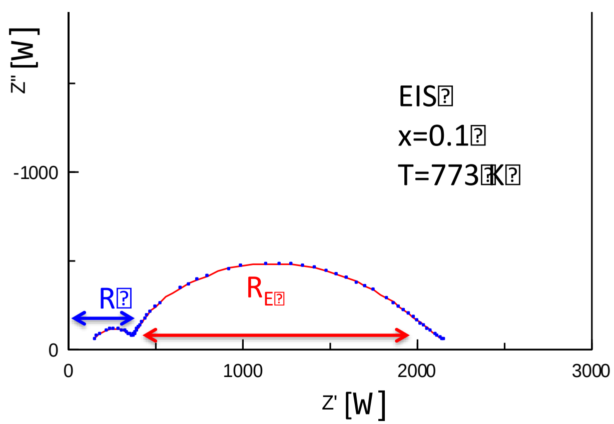
Protonic, Anionic and dual electrolytes for SOFC /SOEC

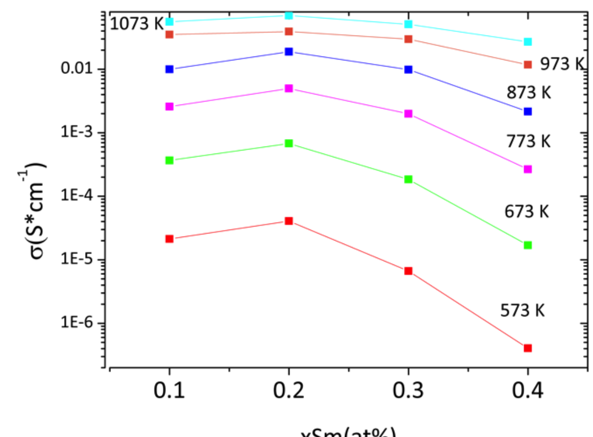




$BaCe_{0.85}Y_{0.15}O_{2.925}$

$Ce_{1-x}Sm_xO_{2-x/2}$



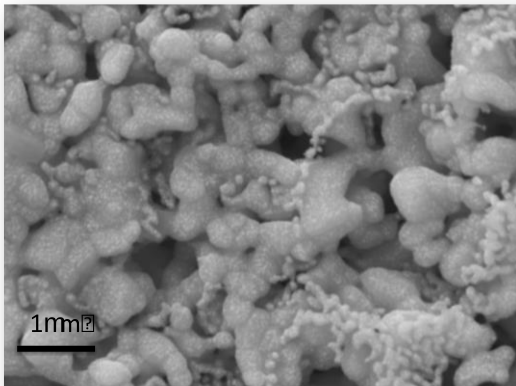


M.Viviani, S.Presto, A. Barbucci, M.P. Carpanese

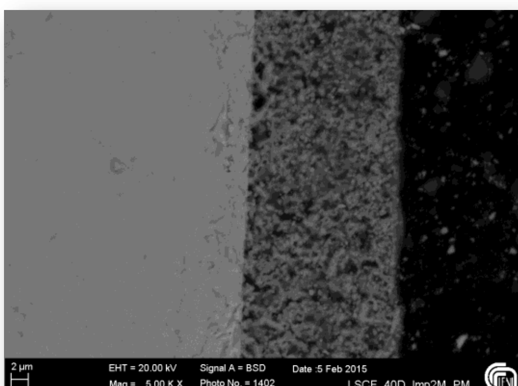
Materials for Electrochemical Energy Conversion

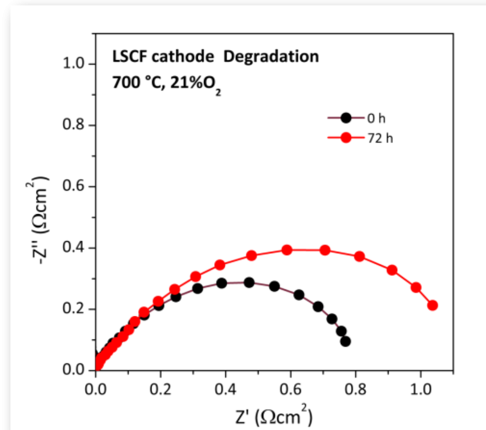
Electrodes for IT-SOFC : impregnated **cathode**

LSM-impregnated LSCF



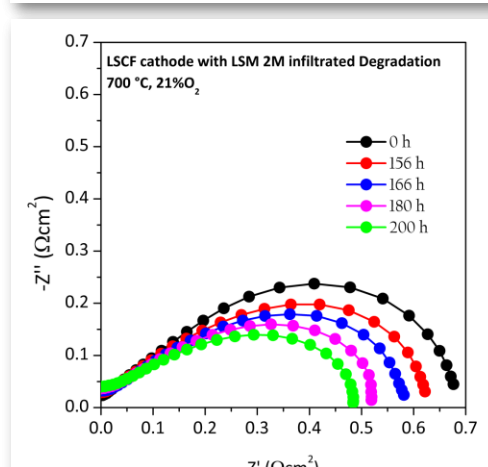
cathode on SDC electrolyte





without impregnation

- higher R_{pol}
- degradation



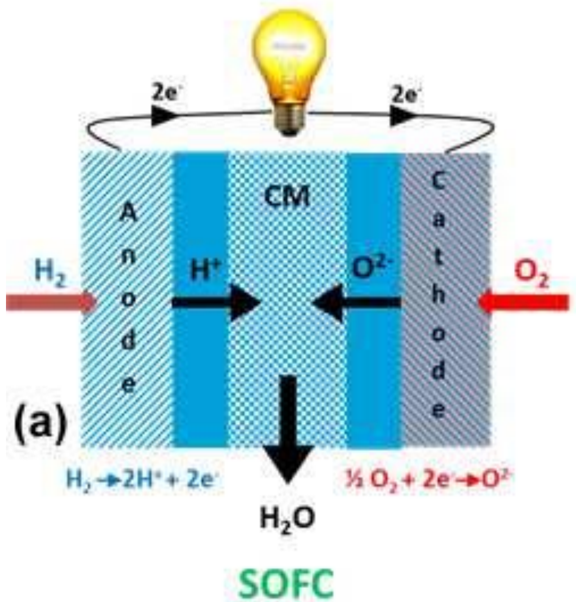
with impregnation

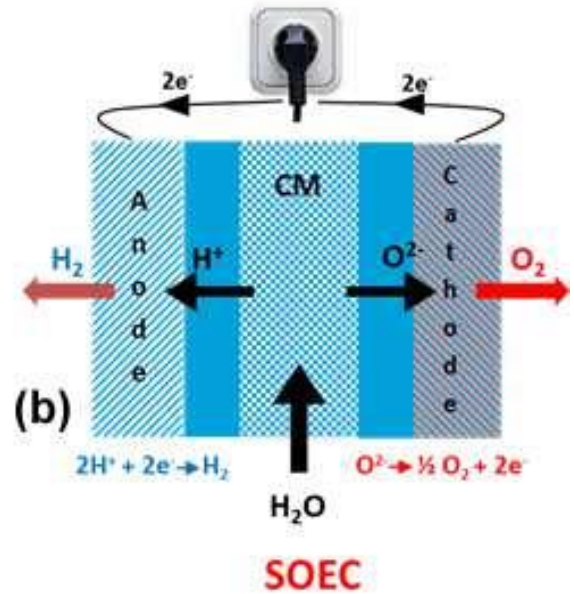
- lower R_{pol}
- no degradation

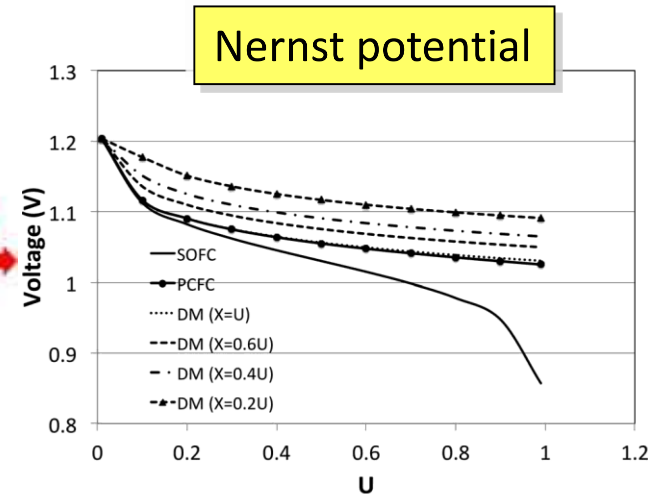
M.Viviani, S.Presto, A. Barbucci, M.P. Carpanese

Materials for Electrochemical Energy Conversion

New architectures: reversible dual cell







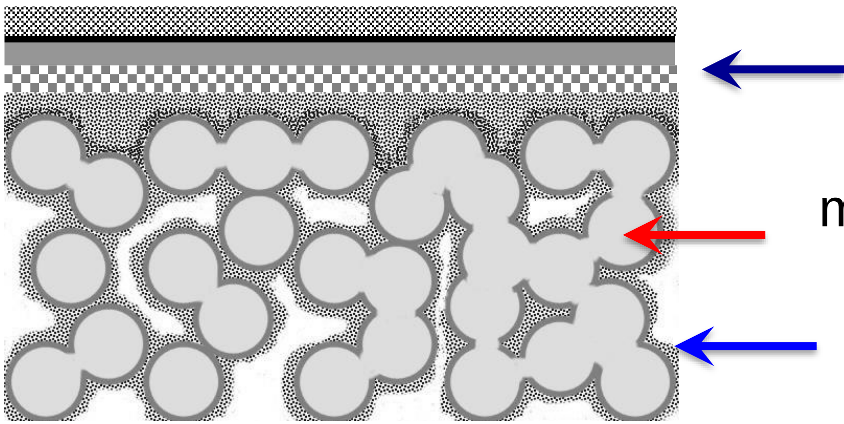
- *no dilution of fuel with H_2O (higher OCV)*
- *stationary conditions in the 3 electrode compartments (* $P_{H_2} = 1;\ P_{O_2} = 1;\ P_{H_2O} = X$)
- *less degradation of interconnects and sealing on H_2 side*
- *fast switching between SOFC/SOEC modes*

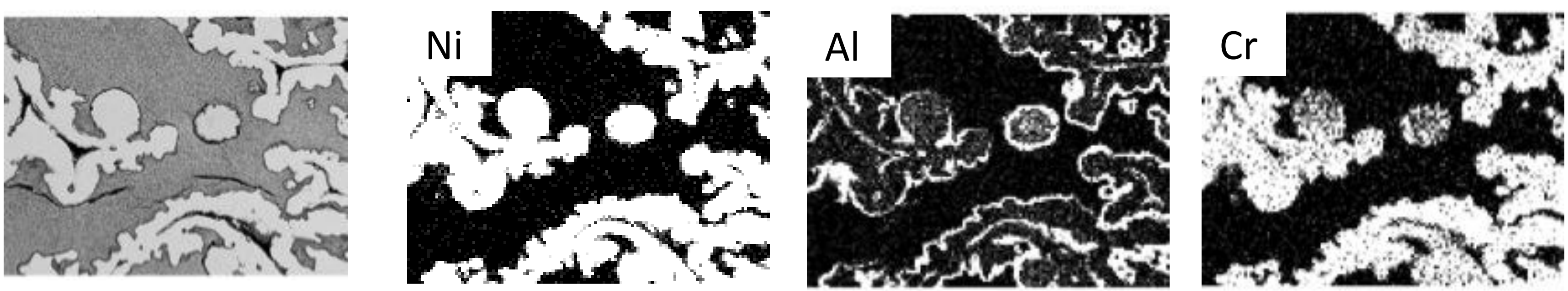
M.Viviani, S.Presto, A. Barbucci, M.P. Carpanese

Materials for Electrochemical Energy Conversion

New architectures: impregnated metal supported SOFC

hybrid current collector/support mechanically and chemically stable under oxidant and reducing atmosphere





M.Viviani, S.Presto, A. Barbucci, M.P. Carpanese

Materiali

interfacce

giunzioni

per l'energia ed applicazioni ad alta temperatura

Surfaces and Interfaces in gas-liquid-solid systems at High Temperature

Materials for Energy: Electrolites foe SOFCs

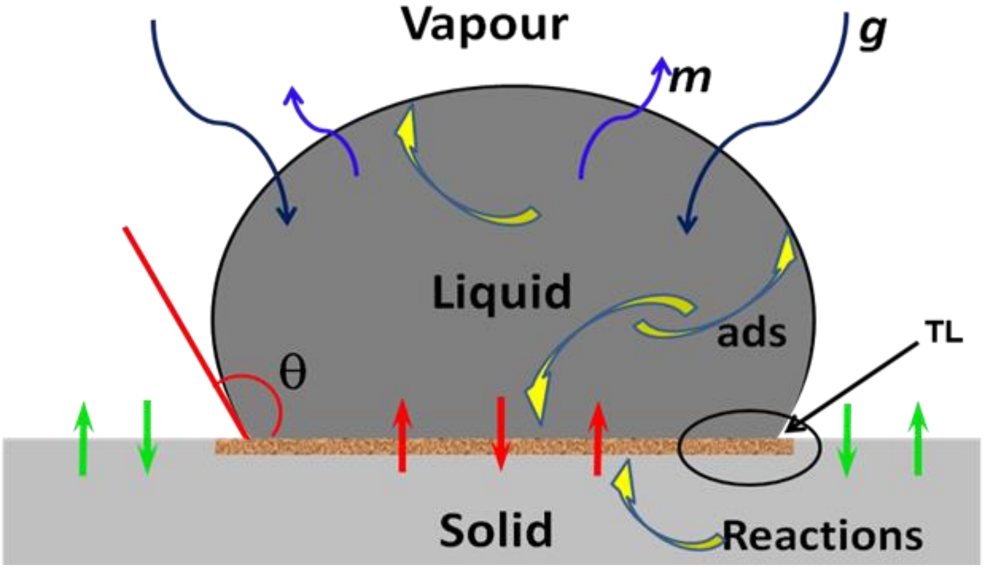
Materials for Electrochemical Energy conversion

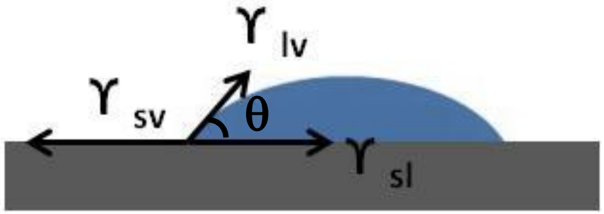
Thermophysical

Corrosion by Liquid

Joining

Interfacial phenomena in liquid metal systems





Υ_{LV} : surface tension of the liquid
θ : contact angle

Young's equation

$$\frac{\gamma_{SV} - \gamma_{LS}}{\gamma_{LV}} = cos\theta$$

Gibbs (isotherm)

$$d\Upsilon = -\Sigma_i \Gamma_i d\mu_i$$

- **S/L interface**

Dissolution of the solid phase, infiltration of the liquid into the solid, formation of interfacial compounds, adsorption of active elements (e.g. Ti, Cr)

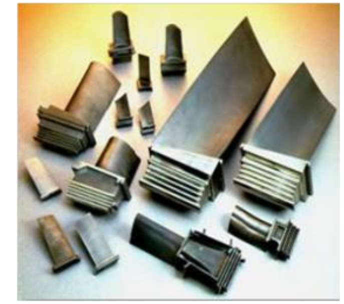
- **L/V interface**

Evaporation, adsorption of gaseous compounds (e.g. oxygen), oxidation

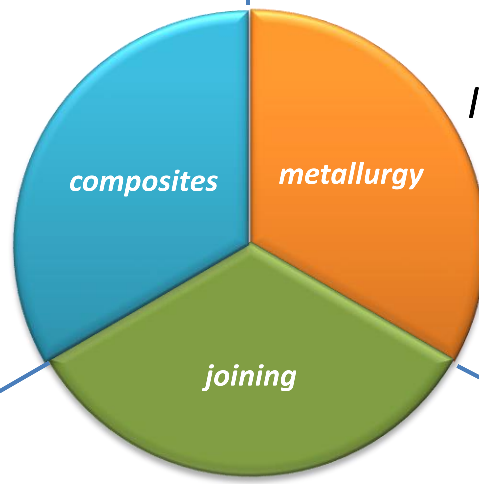
- **S/V interface**

Oxidation-deoxidation of the surface, selective evaporation (e.g. SiO)

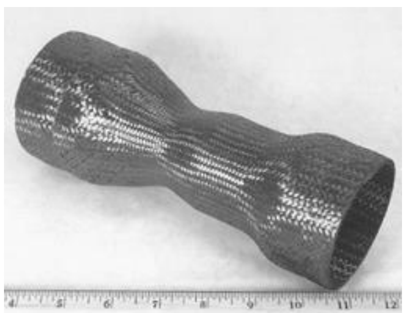
handling of molten metals



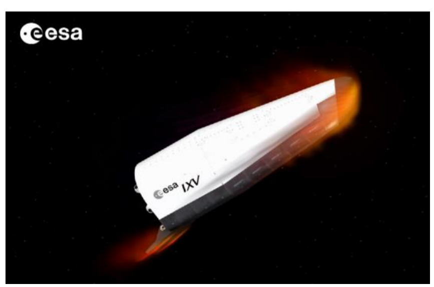
hybrid components by infiltration:
foams
metal-ceramic composites
CMCs SiC/SiC

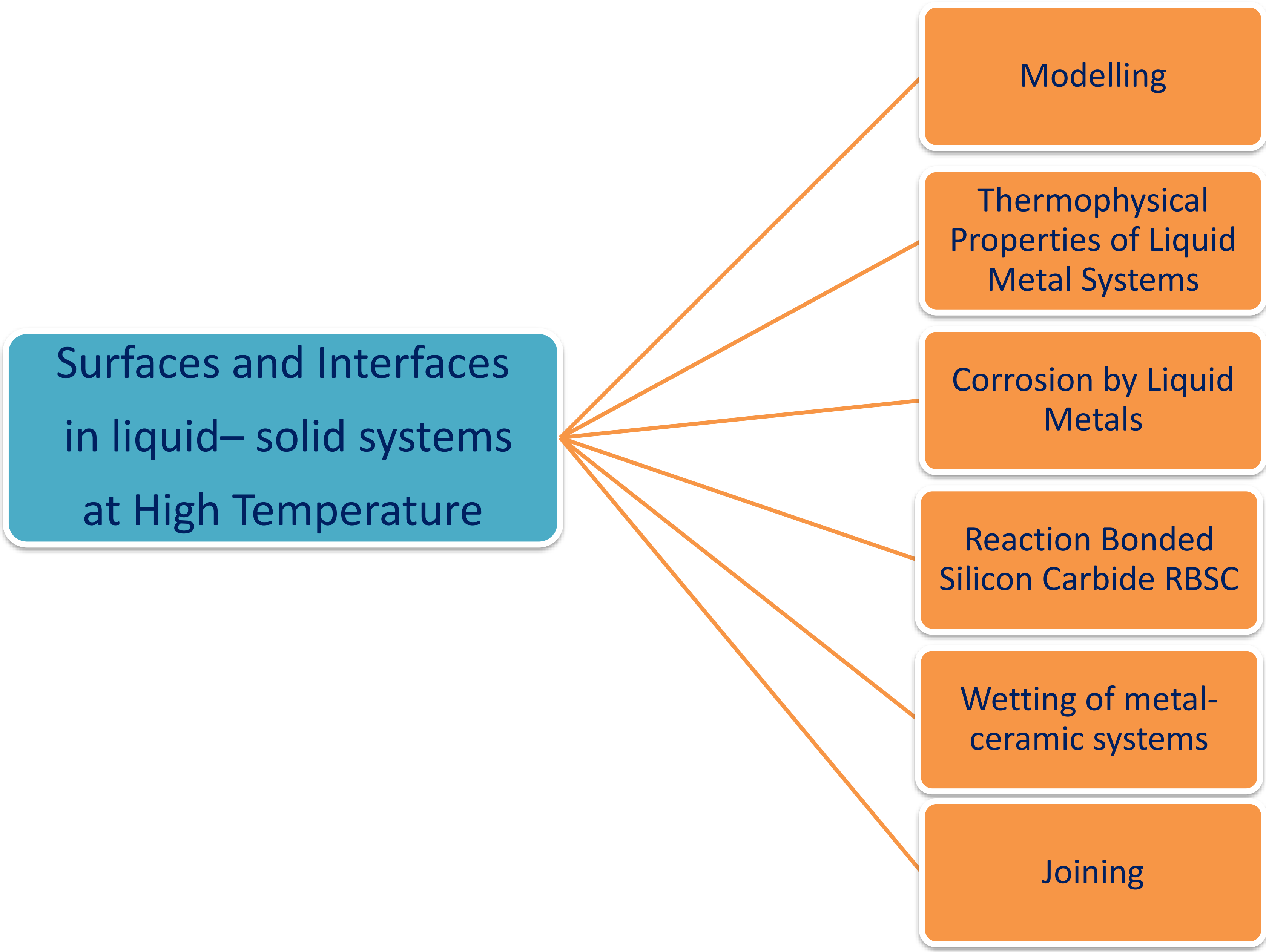


Investment casting of turbine blades



metal-ceramic joining for aerospace, energy production, prosthetic parts, vacuum tight sensors




Surfaces and Interfaces in liquid– solid systems at High Temperature
Modelling
Thermophysical Properties of Liquid Metal Systems
Corrosion by Liquid Metals
Reaction Bonded Silicon Carbide RBSC
Wetting of metal-ceramic systems
Joining

Modelling

Rada Novakovic

Surfaces and Interfaces in liquid– solid systems at High Temperature

- Thermophysical Properties of Liquid
- Corrosion by Liquid Metals
- Reaction Bonded Silicon Carbide RBSC
- Wetting of metal-
- Joining

Presentazione Junior - *Donatella Giuranno*
Modellizzazione delle proprietà chimico-fisiche di superficie e di bulk dei materiali: attività attuali e potenzialità

POSTER P13

Modelling and simulation of metallic systems: Thermodynamic, Statistical mechanics & Kinetic Theory of Matter approaches

1. Phase diagrams optimization by CALPHAD method

2. Prediction of thermophysical properties of metallic melts:
   - 2.1 surface properties (surface tension & surface segregation)
   - 2.2 dynamic properties (diffusion, viscosity, electrical resistivity)
   - 2.3 microscopic functions (concentration fluctuations & short range ordering)

3. Study of oxidation phenomena at the surface of metallic melts:
   Fluido-dynamic model

4. Modelling of microstructure evolution of liquid / solid interface:
   Phase field method

5. Studies on "Small systems" (nanosized particle > 4 nm)
   - 5.1 Calculations of nanosized Phase diagrams (extended CALPHAD method)
   - 5.2 Melting temperature depression
   - 5.3 Coalescence / aggregation of nano-sized particles

Models Framework: Home-made software in Matlab and/or Commercial software

Surfaces and Interfaces in liquid– solid systems at High Temperature

- Modelling
- Thermophysical Properties of Liquid Metal Systems
- Corrosion by Liquid Metals
- Reaction Bonded Silicon Carbide RBSC
- Wetting of metal-
- Joining

Donatella Giuranno
Rada Novakovic
Enrica Ricci

Associati:
Elisabetta Arato
Gabriella Borzone
Simona Delsante

Thermophysical Properties of Liquid Metal Systems –P21

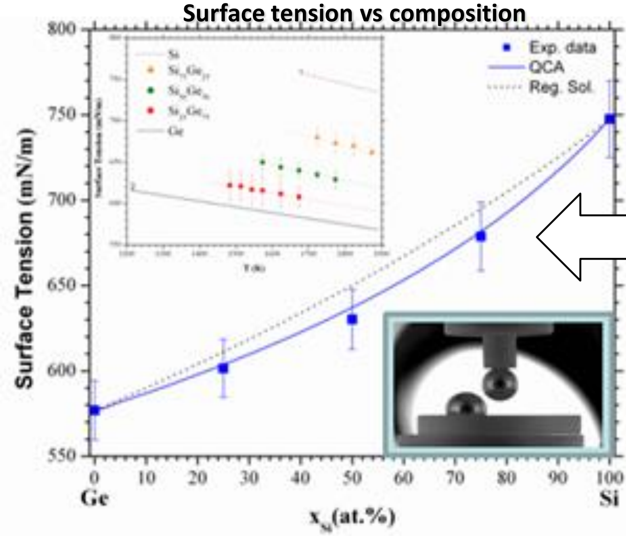
Ente finanziatore: ESA e ASI

Collaborations: DLR, UNI-ULM, UNI -TO, CNRS, EMPA, UNI-Alberta, UNI-Warwich, AREVA, NETZSCH,TATA, Jaxa, Tokyo University…

Combined experimental-theoretical method aiming to study the thermophysical properties, the reactivity and the relationships with microstructure evolution of molten melts

Si-Ge system

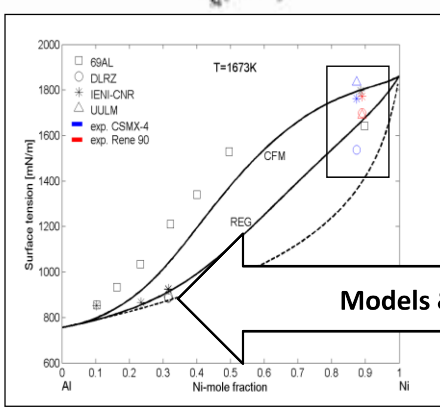
Surface tension vs composition

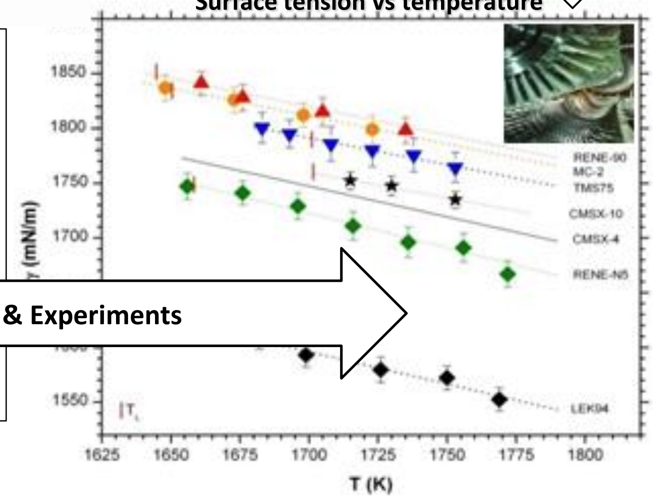


μg vs 1g

Ni-based Superalloys

Surface tension vs temperature





Models & Experiments

Al-Ni: CFM, QCA, SA models

Surface tension isotherms

GOALS:

- ✓ **Optimization of industrial processes**
- ✓ **Design of new materials for HT appl.**

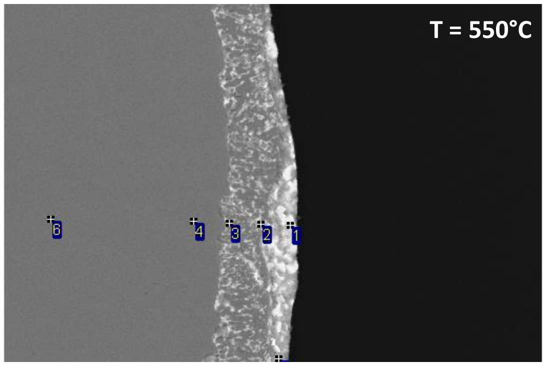
Systems investigated:

- ❑ Al-Ni intermetallics (Fuel Cell catalysis; Turbines, etc..)
- ❑ Al-Ti based alloys (Turbines-casting process; Aerospace appl.)
- ❑ Cu based alloys (Micro-electronics…..)
- ❑ Sn-rich alloys (Solders)
- ❑ Ni based superalloys (Power generation components etc….)
- ❑ Si alloys (Semiconductors; composites)
- ❑ Cu-Zr based alloys (HEA; BMG…)

Corrosion by liquid metal (Pb / PbBi eut) of ferritic/martensitic and ODS steels

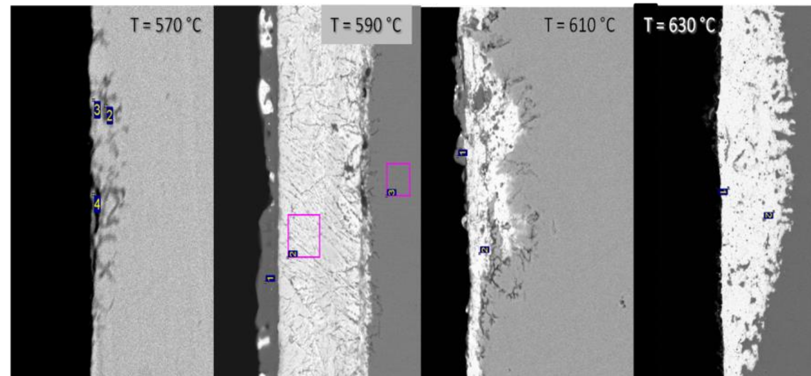
Ente finanziatore: EU-EURATOM | **Collaborations: CNR-IFP, KIT, CEA, CIEMAT, ENEA....**

Qualification of reference materials for the Gen IV reactors with particular attention to the italian concepts of Lead Fast Reactor (LFR)



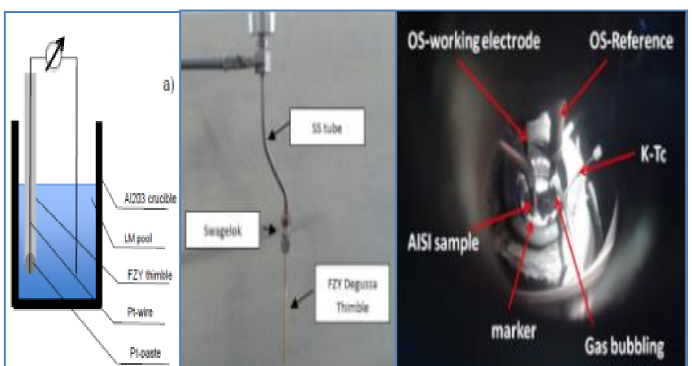
Corrosion of AISI 316 steel by liquid LBE after 1500 h under an Ar/H_2 atmosphere

The analysis of the corrosion behavior of different structural materials in contact with liquid Pb and LBE (coolants), allows a proper selection of materials and procedures for the HLM technologies.

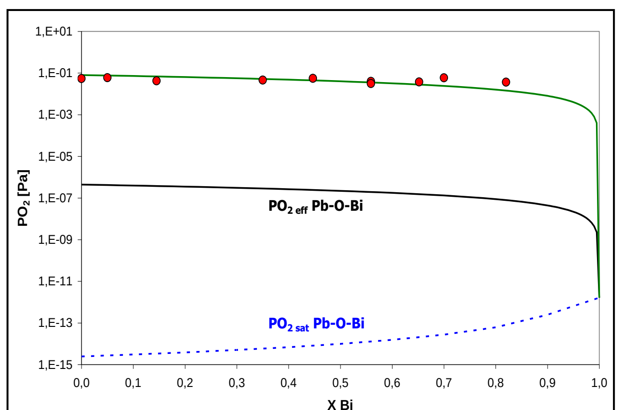


Corrosion of T91 steel by liquid Pb after 550 h under an Ar atmosphere

For the understanding of corrosion mechanisms, the study of the chemistry of heavy liquid metals through the monitoring and **the control of the dissolved oxygen** is fundamental.



Development of an electrode for the control and monitoring of oxygen content in the liquid metal bath



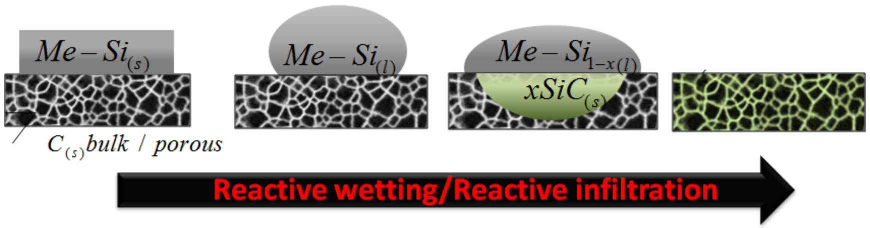
Phisico-chemical conditions of oxidation regimes for the Pb-O-Bi system

Alternative solutions are required to overcome the corrosion effects such as surface protective films

See collaboration with Padoa Group and CNR IFP (**POSTER**)

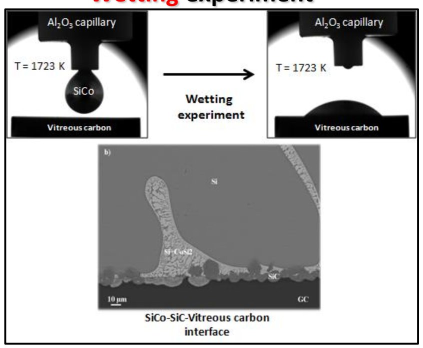
Reaction-Bonded Silicon Carbide (RBSC)

Collaborations: Instituto Universitario de Materiales de Alicante (IUMA), Universidad de Alicante



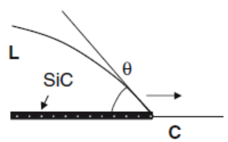
Combined **experimental-theoretical** method aiming to study the **kinetics of reactive infiltration of Me-Si alloys into C-porous materials** and to determine the **elementary process limiting the infiltration rate**

Combined **Surface tension** and **Wetting** experiment

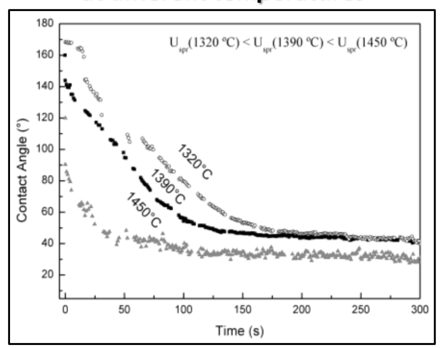


SiCo-SiC-Vitreous carbon interface

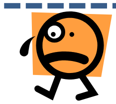
Reaction-controlled wetting



Spreading kinetics of $Si_{62.5}Co_{37.5}$ / GC at different temperatures



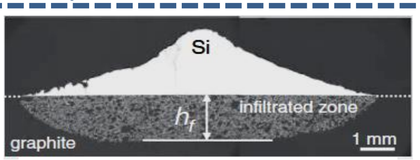
Washburn's Eq. $h^2 = r_{\mathrm{eff}}\dfrac{\sigma\cos\theta}{2\eta}t$



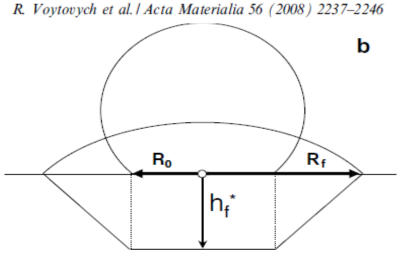
"porous closer"

GOALS:

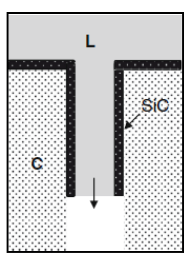
- ✓Production of improved SiC/Me_xSi_y composites
- ✓Design of new materials for :
- ✓M-EHT Applications
- ✓light-weighting
- ✓Electronics
- ✓Breaking systems
- ✓anti-ballistic shields, etc.



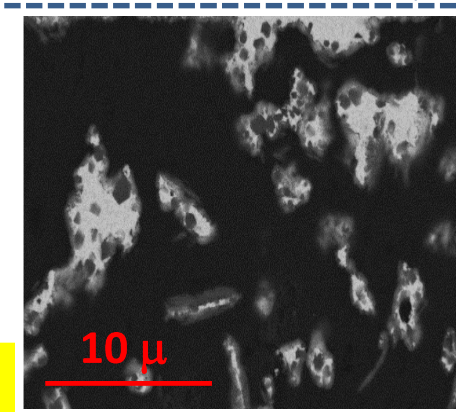
R. Voytovych et al. / Acta Materialia 56 (2008) 2237–2246



Schematic drawing of **Infiltration**



Reaction-controlled infiltration



Infiltrated area (Si-Ir/C-porous graphite)

Systems under study:

C-materials/porous preforms

HOPG, GC

Graphite, C-fibers, C/SiC

Me-Si alloys

Si, Si-Co, Si-Ir, Si-Zr, Si-Mo, Si-V.

Surfaces and Interfaces in liquid– solid systems at High Temperature

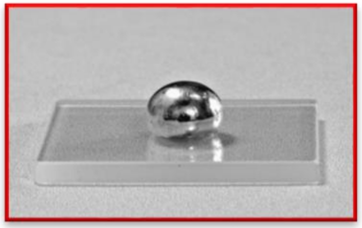
- Modelling
- Properties of Liquid
- Reaction Bonded
- Corrosion by Liquid Metals
- Wetting of metal-ceramic systems
- Joining

Sofia Gambaro
Maria Luigia Muolo
Alberto Passerone
Fabrizio Valenza

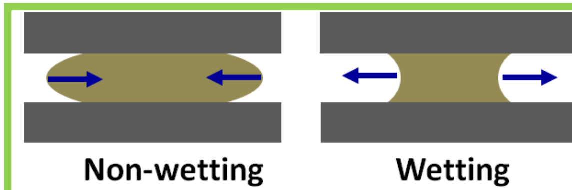
Associati:
Cristina Artini
Gabriele Cacciamani

Wetting of Metal-Ceramic Systems

1. Analysis of wetting



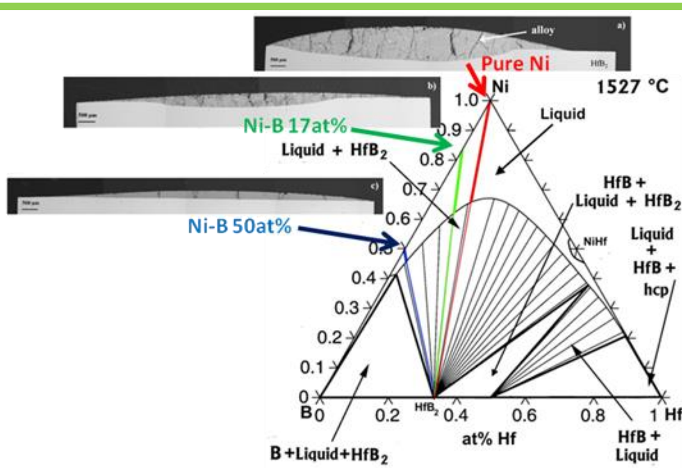
sessile drop after cooling (θ>90°)



A braze alloy relies on capillarity to distribute the liquid alloy along the adjoining interfaces

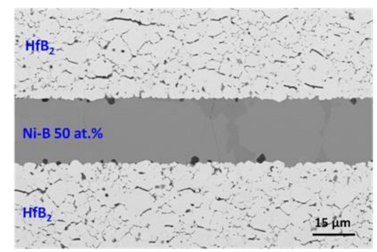
sessile drop during test (θ<90°)

2. Thermodynamic assessment of the interface



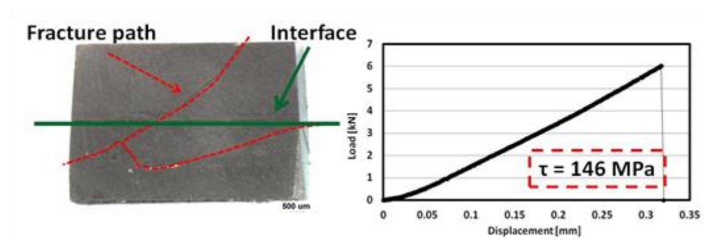
Interfacial microstructures of cross-sectioned wetting samples in relation to phase diagram

3. Manufacturing of joined specimens



Example of HfB_2/HfB_2 joint

4. Mechanical characterization: shear test



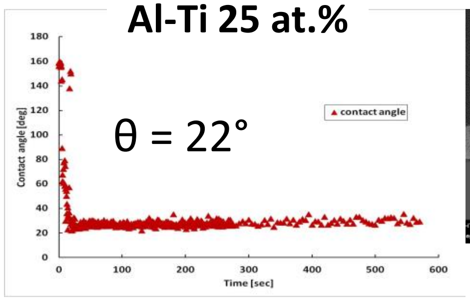
Joined samples after rupture test andload displacement curve

Bonding procedures for SiC-SiC composites for aerospace –P39

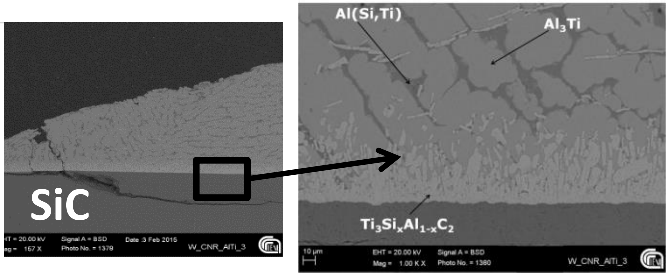
<u>Target application</u>: bodyflaps for **ESA IXV** experimental re-entry vehicle (assembly of CMCs in complex parts)

<u>Methodology pursued:</u> advanced brazing through metallic interlayers (e.g. Al-Ti, Co-Ta, Ni-Ta)

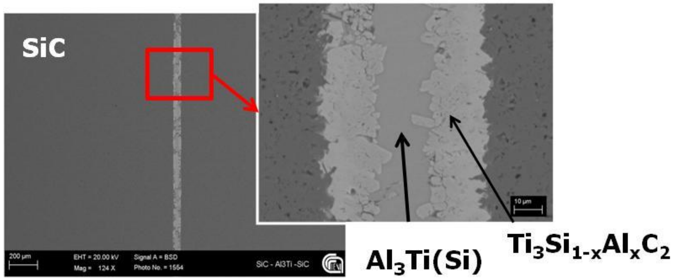
CMCs bodyflaps in ESA IXV



Kinetics of wetting



Interfacial microstructure



Joint obtained by Al-Ti: cross section

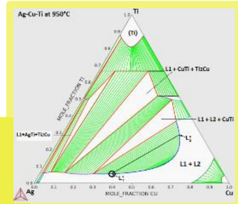
- Good wetting of Al-Ti alloys on SiC.
- Formation of interfacial $Ti_3Si_{1-x}Al_xC_2$ whose melting point is over the testing temperature: good for high temperature applications.

Project ADMACOM (Advanced manufacturing routes for metal/composite components for aerospace, www.admacomproject.eu, EU-FP7 2007-2013, grant agreement 609188).

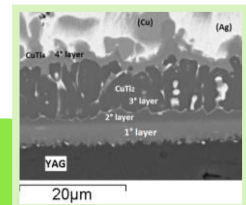
ADMACOM
POLITECNICO DI TORINO
Politecnico di Torino (POLITO)
MT AEROSPACE
MT Aerospace AG
AIRBUS GROUP
Airbus Group Innovations
Fraunhofer IFAM
Fraunhofer IFAM
EMPA Materials Science & Technology
Swiss Federal Laboratories for Materials Science and Technology
IENI
Consiglio Nazionale delle Ricerche - IENI
NANOforce
NanoForce Technology Ltd

Metal-ceramic joints: Brazing transparent YAG to Ti6Al4V

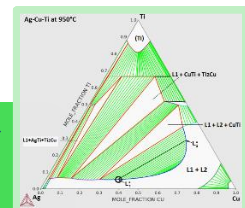
$Y_3Al_5O_{12}$ produced by ISTEC-CNR
Ag-based filler alloys
Ti6Al4V metallic support



Thermodynamic approach CALPHAD

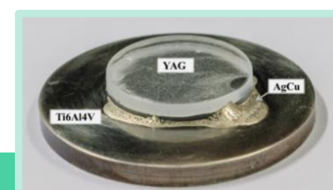


Wetting tests + microstructural characterization by SEM-EDS



Validation of interfacial reactivity by CALPHAD – Phase Diagram

Selection of the best brazing alloy composition



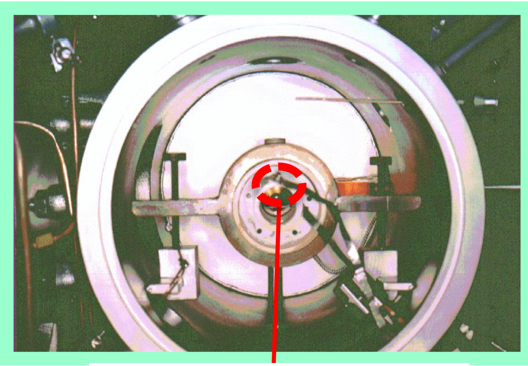
Production of test joints

Small prototypes for mechanical, vacuum and sea water tests

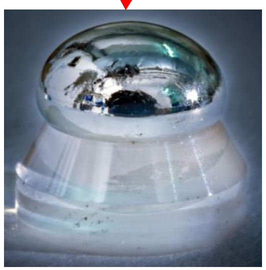
Presentazione Junior
Sofia Gambaro

Ritmare
La ricerca italiana per il mare

HIGH TEMPERATURE TENSIOMETRIC LABORATORY

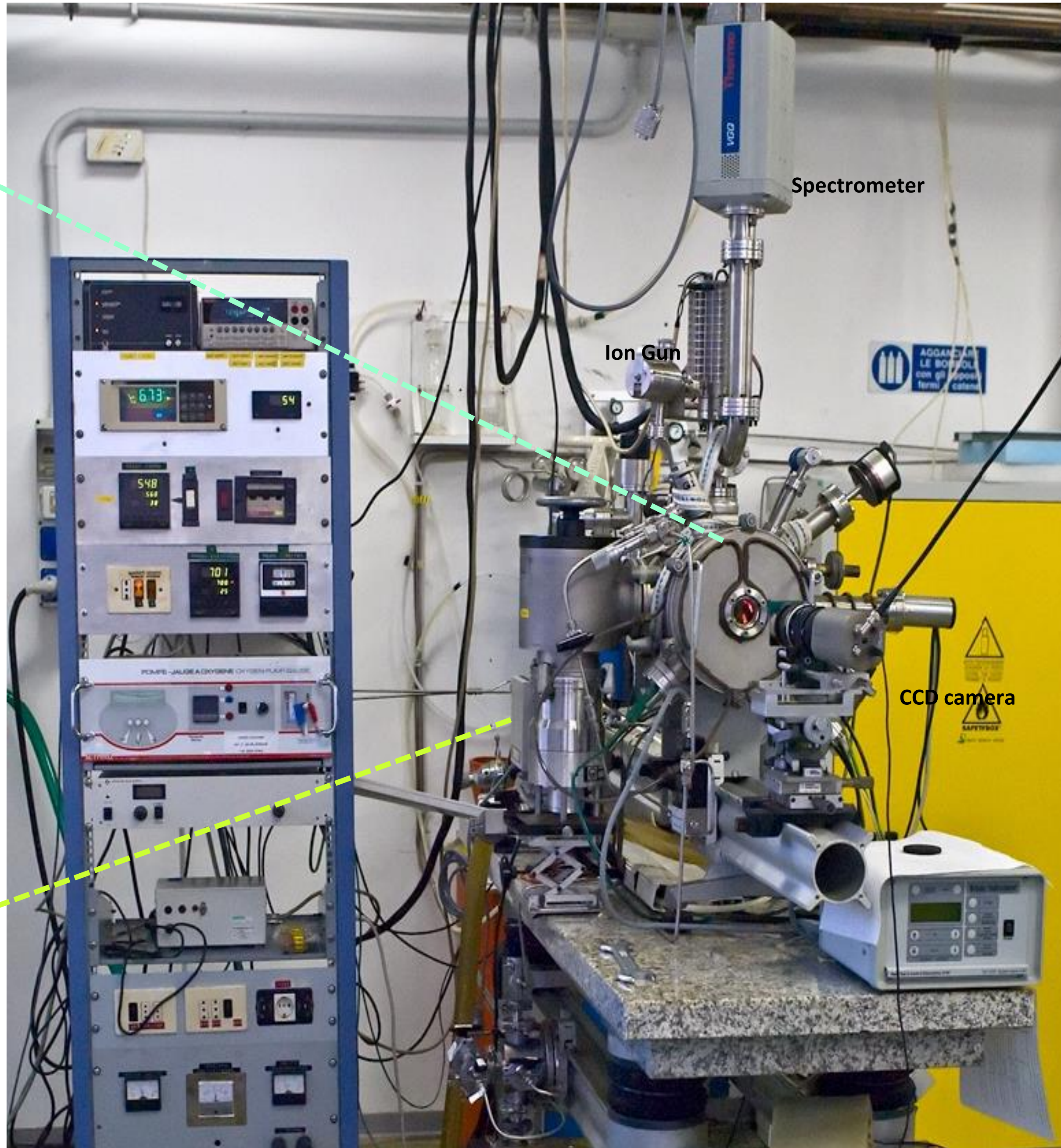


Internal view of Pt furnace



Liquid metal sample on sappphire crucible
(Large Drop method)

Zirconia sensors to control amd measure the
Oxygen Partial Pressure

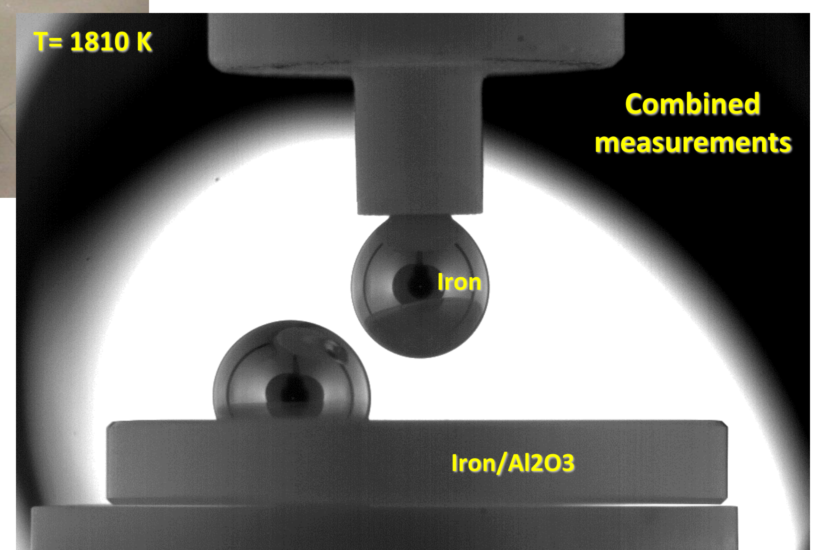


VERY HIGH TEMPERATURE TENSIOMETRIC LABORATORY

in collaboration with

Foundry Research Institute. Cracow (P)

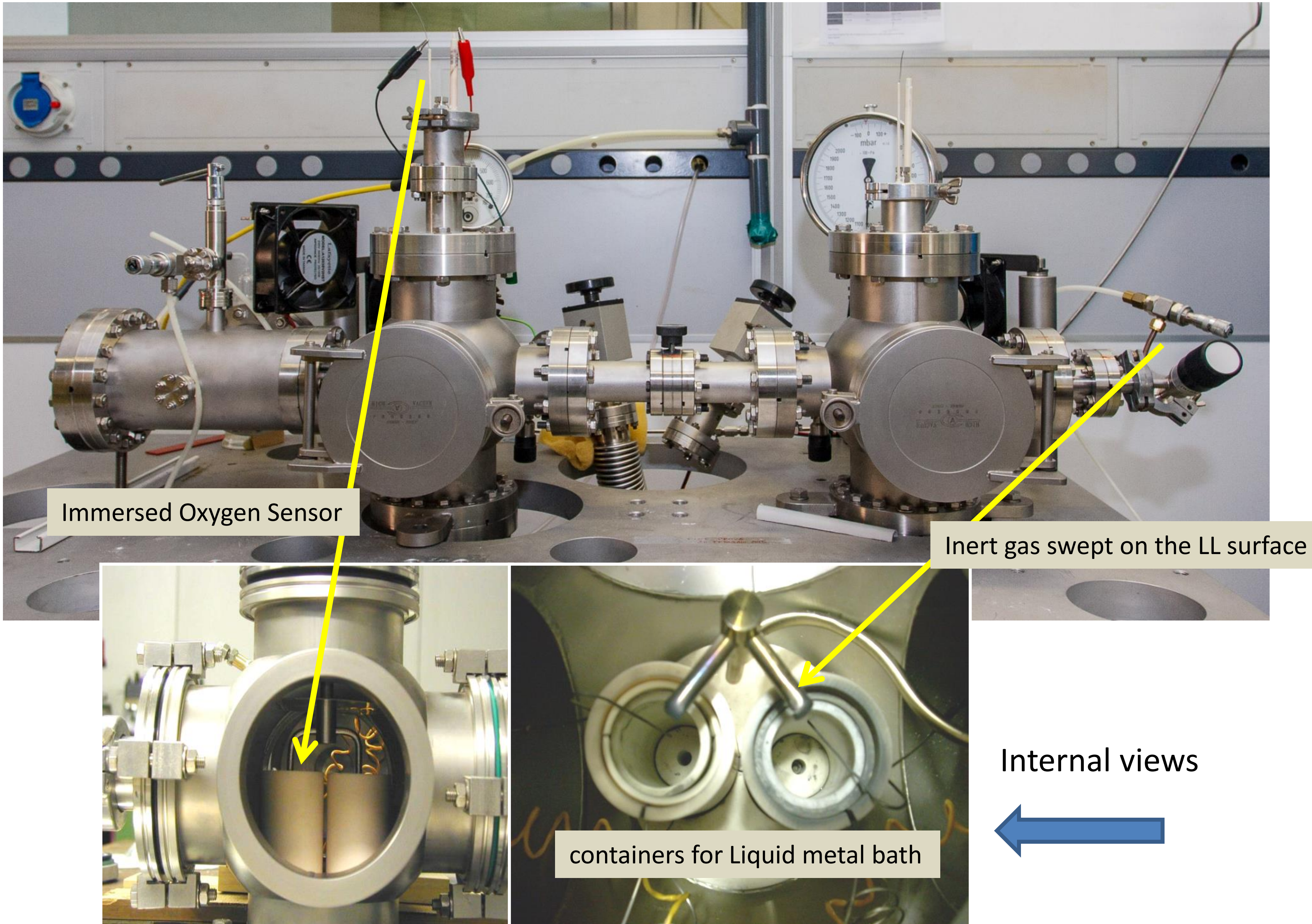
- ✓ Experimental temperature: up to 2100ºC
- ✓ Manipulators for movement of samples, capillary and support
- ✓ 3 thermocouples for temperature control
- ✓ Real-time residual gas analysis
- ✓ Methods applicable:
  Sessile drop+Pendant drop
  +Tranferred drop



Advantages:

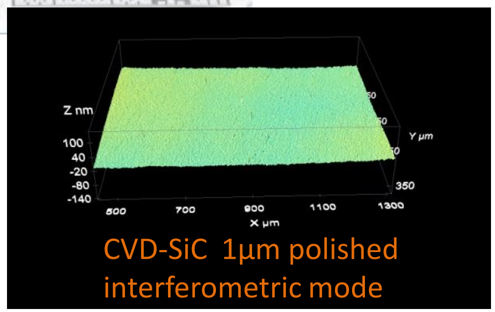
- Capillary purification of the drop during its formation
- Smaller contact area between container (capillary) and liquid metal (quasi containerless method)

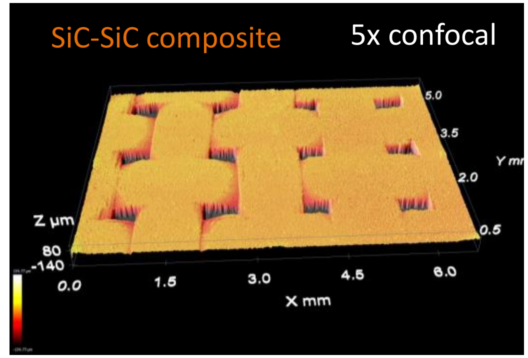
CORAL : Corrosion Apparatus for Liquid Metal

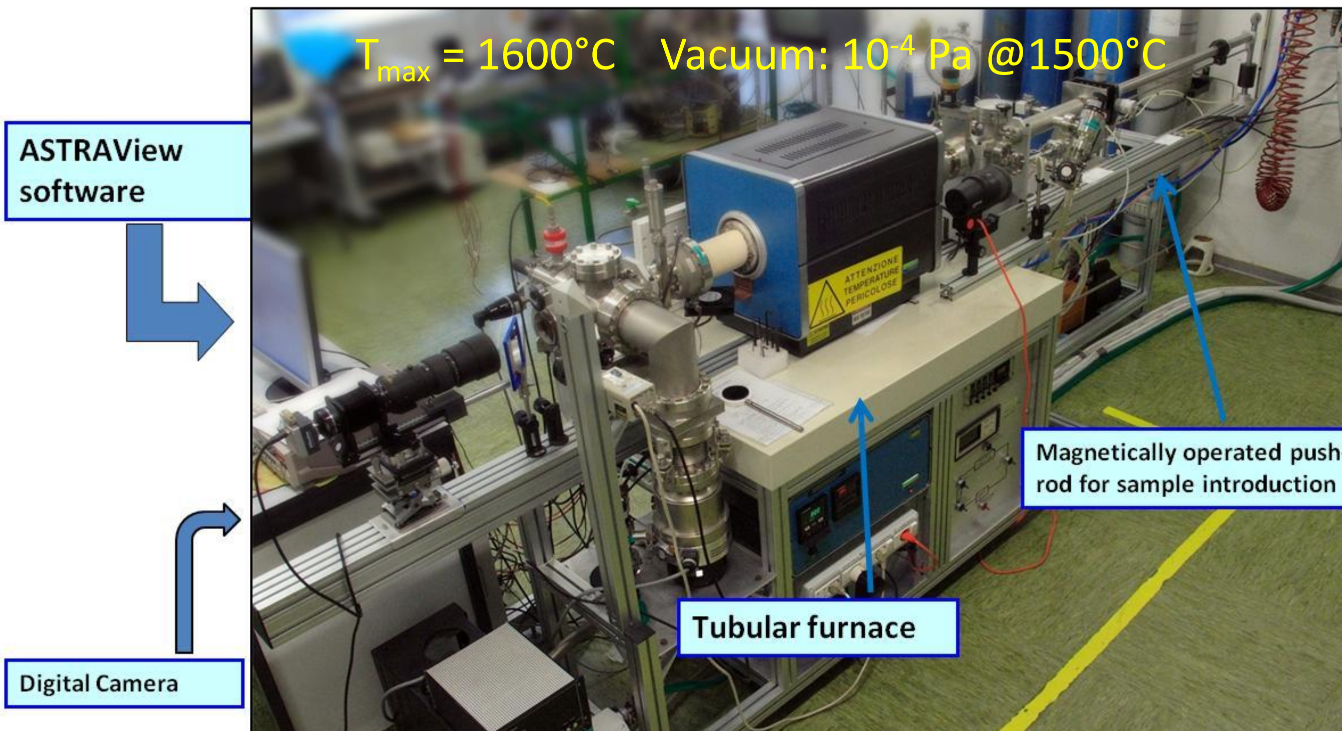


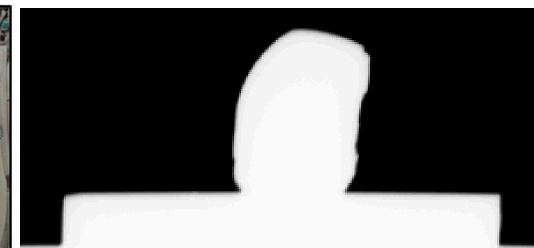
Internal views

Experimental apparatus for wetting tests

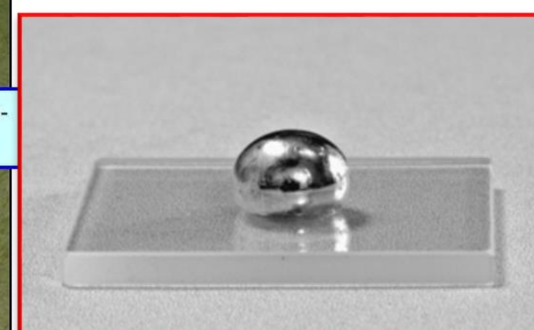








sessile drop during test (θ<90°)



sessile drop after cooling (θ>90°)

Materiali, interfacce e giunzioni per l’energia ed applicazioni ad alta temperatura

Grazie

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