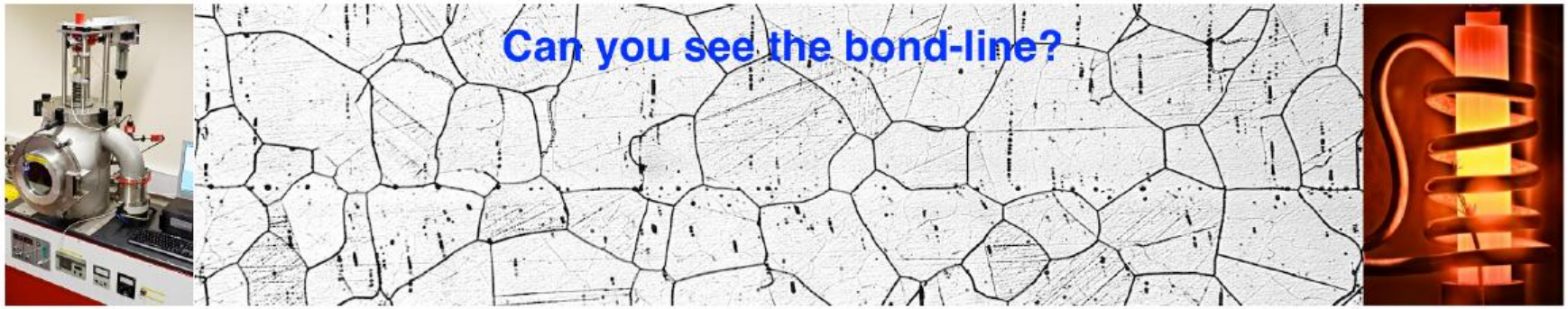
The Open University

Symposium of

World Experts in Diffusion Bonding (WEDB)

The Open University, United Kingdom

20-21 June 2017



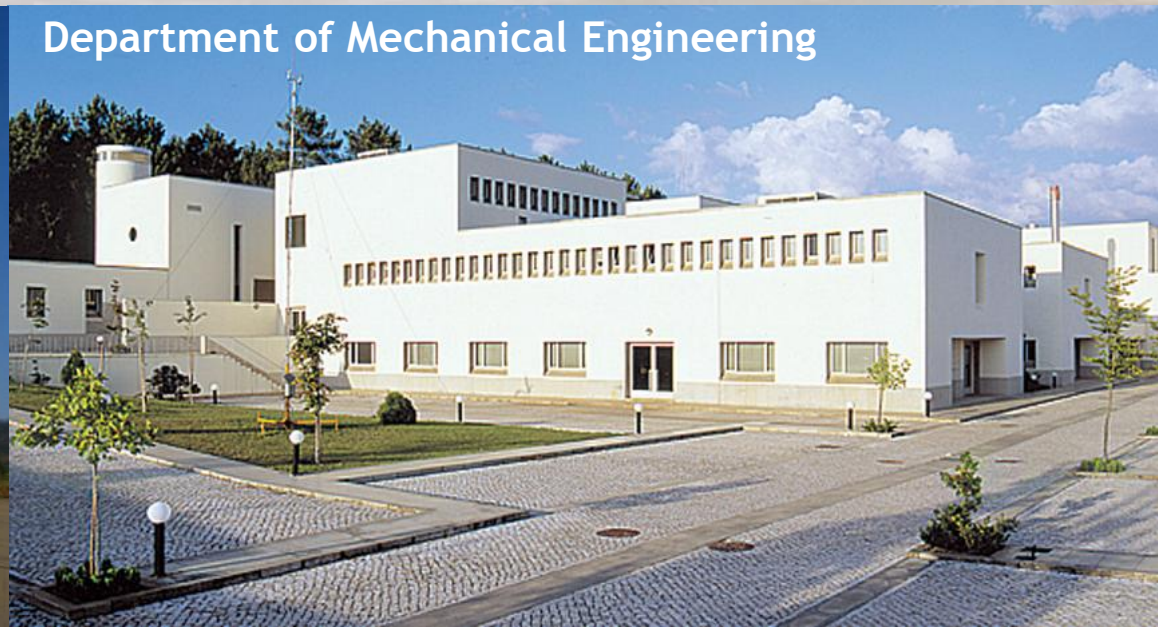
Ana Sofia Ramos

UNIVERSITY of COIMBRA

Video UC.mp4

Faculty of Sciences & Technology

Department of Mechanical Engineering



CEMMPRE

Centre for Mechanical Engineering, Materials and Processes

University of Coimbra

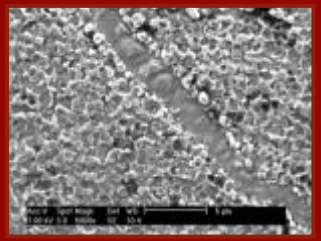
University of Trás-os-Montes e Alto Douto

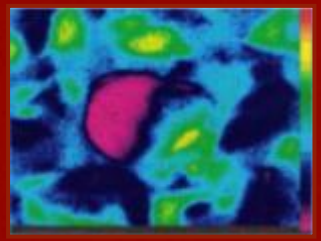
University of Porto

responsible
Bruno Trindade

CEMMPRE

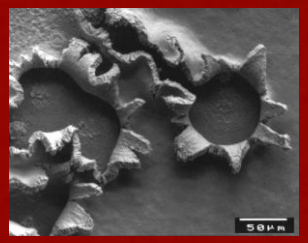
- **The Centre for Mechanical Engineering, Materials and Processes, CEMMPRE (ex CEMUC- Centre for Mechanical Engineering of the University of Coimbra) is an interdisciplinary R&D Research Unit of the Portuguese Foundation for Science and Technology and currently comprises 114 researchers with PhD degree in different scientific domains.**
- **The thematic lines of CEMMPRE cover the whole advanced material cycle from raw materials to final product, including advanced processing systems, simulation, chemical, physical, structural and mechanical characterisation of the materials and their components, industrial robotics and product management.**

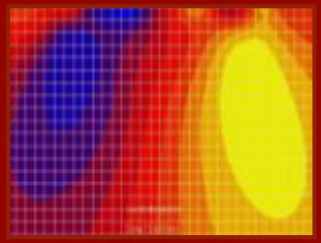




CEMMPRE

scientific groups

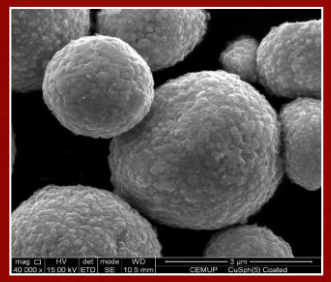


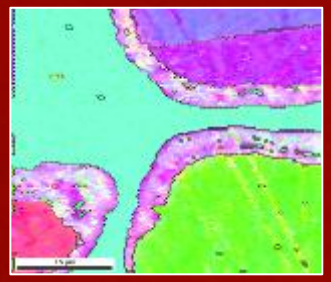


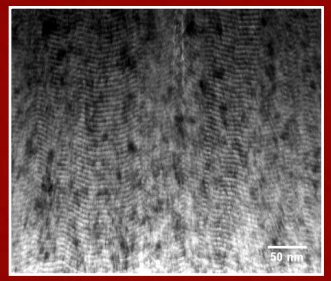
- Advanced manufacturing systems;
- Bioengineering & polymer synthesis;
- Mining & raw materials;
- **Nanomaterials & Micromanufacturing**;
- Sensors and nanoelectrochemistry;
- Structural integrity;
- Surface engineering.

NANOMATERIALS & MICROMANUFACTURING

Principal Investigator – Teresa Vieira







The main fields of expertise in the group can be summarized as follows:

- 2D/3D powders: new materials for mobility (transports, energy and health devices) using sputtering and milling;
- Micromanufacturing applied to inorganic materials/powders:
- MicroPIM;
- New replicative process such as hot-embossing; additive processes;
- **Joining using reactive nanomultilayers;**
- New sintering processes;
- Development of new solutions for improvement quality of life;
- Valuation/remediation and protection of contaminated industrial or mining environments (toxic elements and nanoparticles).

REACTION-ASSISTED DIFFUSION BONDING OF DISSIMILAR MATERIALS

A.S. Ramos[1], S. Simões[2], A.J. Cavaleiro[1], F. Viana[2], M.F. Vieira[2], J. Morgiel[3], M.T. Vieira[1]

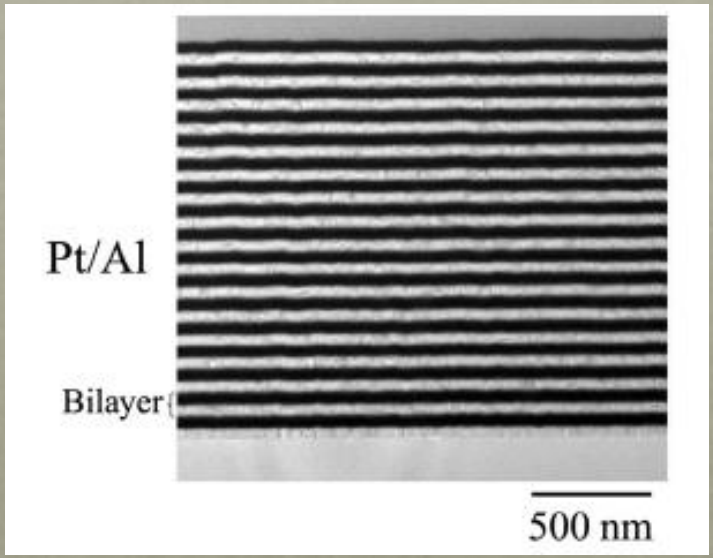
[1]CEMMPRE, Department of Mechanical Engineering
University of Coimbra, PORTUGAL
[2]CEMMPRE, Department of Metallurgical and Materials Engineering
University of Porto, PORTUGAL
[3]Polish Academy of Sciences, POLAND

OUTLINE

- Motivation
- As-deposited multilayer thin films
- Structural evolution
- Heat treated films
- Reaction-assisted diffusion bonding
    - Similar
    - Dissimilar
- Summary

MOTIVATION – Reactive Multilayers

"A reactive multilayer (ML) is a relatively new form of ***energetic material*** that consists of a well-defined, heterogeneous structure and stored chemical energy. These metastable solids are composed of alternating layers of at least two reactants, with total thickness in the range of ~0.1 to 300 μm. The majority of reactant pairs that make up MLs are characterized by a large heat of formation and high adiabatic reaction temperature."



TEM image of a Pt/Al multilayer
(94 nm bilayer thickness)

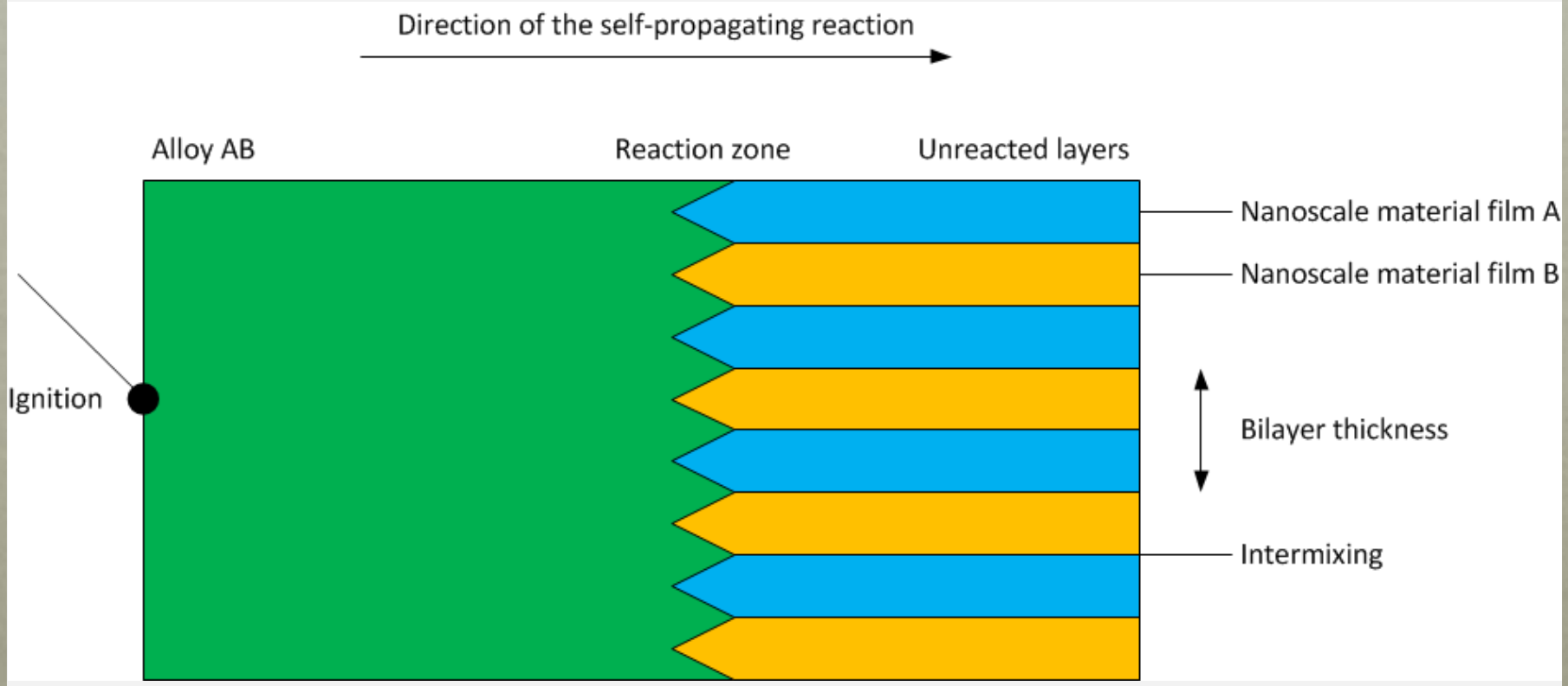
In nanoscale multilayers the diffusion distances are reduced and heat can be generated faster, increasing the reaction velocity and enabling exothermic reactions to become self-sustained in several systems.

More than 50 Me/Me, Me/semiconductor, Me/metalloid, Me/Me-oxide systems have been reported, with most MLs fabricated by magnetron sputtering or electron-beam evaporation.
These MLs react either by thermal explosion or by self-propagation.

D.P. Adams, Thin Solid Films 576 (2015) 98

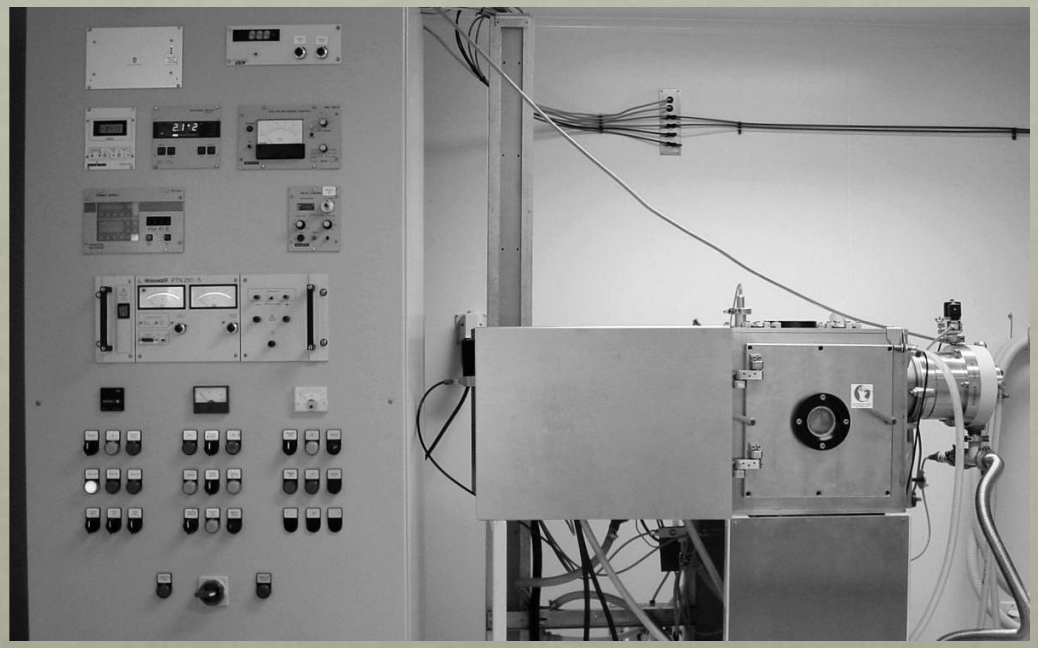
MOTIVATION – Reactive Multilayers

self-propagating reaction in a multilayer system after ignition



ECS Transactions **33** (2010) 307

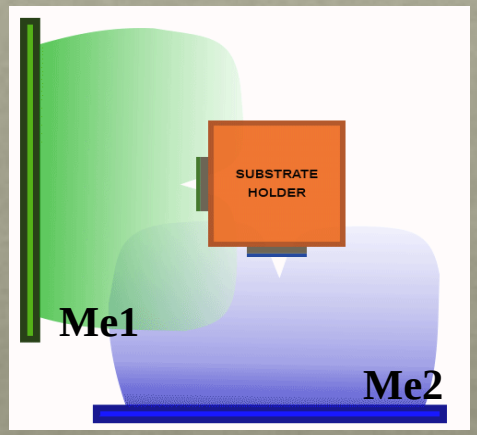
REACTIVE MULTILAYERS – DEPOSITION TECHNIQUE



- DC magnetron sputtering
- High purity Me1 and Me2 targets
- Base pressure < 5×10^{-4} Pa
- P = 0.3 – 0.4 Pa
- Substrate bias = -40 V
- Total thickness ≈ 2.5 μm
- Periods (Λ) between 4 and 200 nm

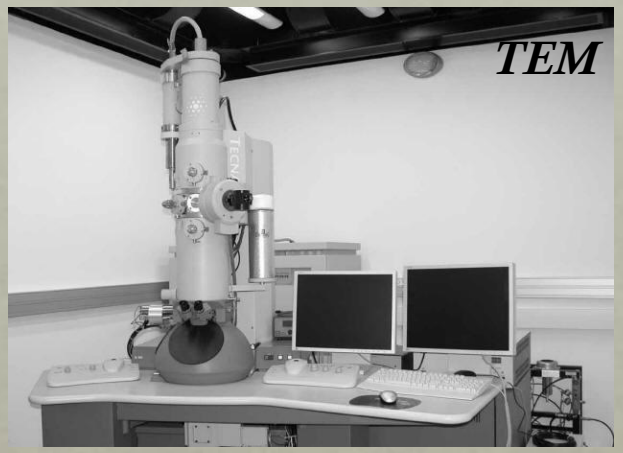
$$\Lambda = \frac{t}{d.rp}$$

t – thickness
d – deposition time
rp – substrates' rotation speed



CHARACTERIZATION TECHNIQUES

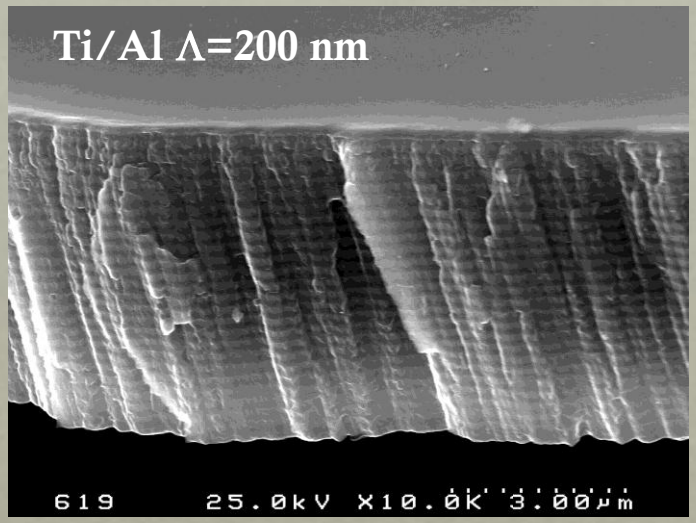
Scanning Electron Microscopy

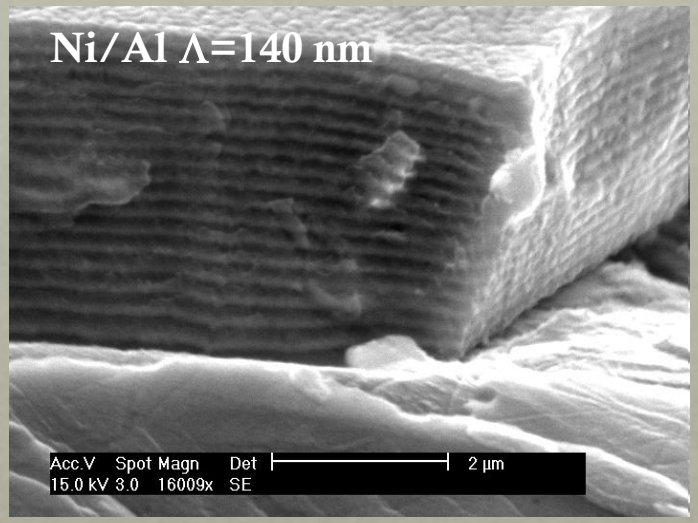


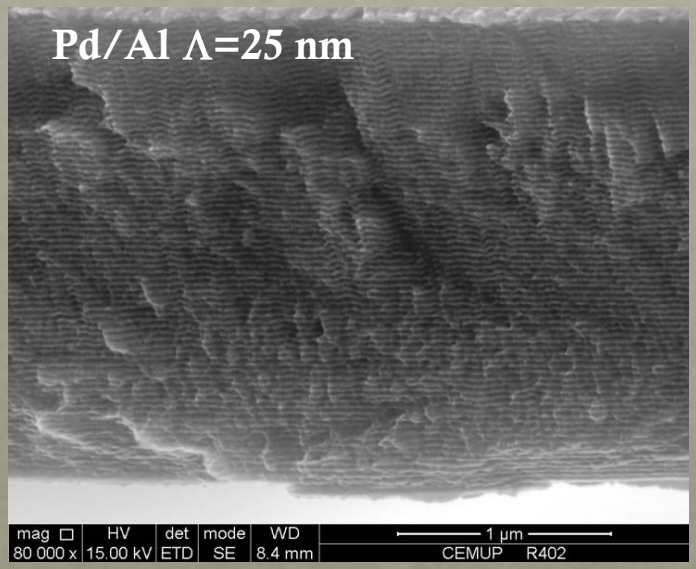
Transmission Electron Microscopy

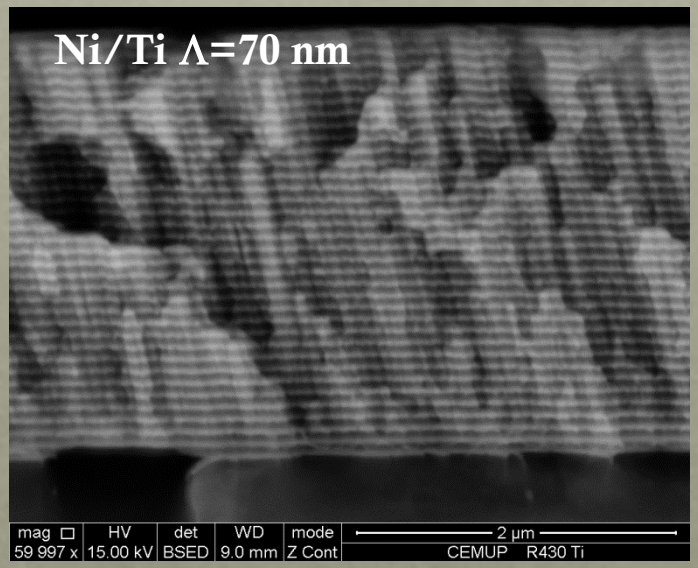
Thermal Stability
- Differential Scanning Calorimetry
- X-ray Diffraction using:
  - Cobalt radiation
  - Synchrotron radiation

AS-DEPOSITED MULTILAYER THIN FILMS







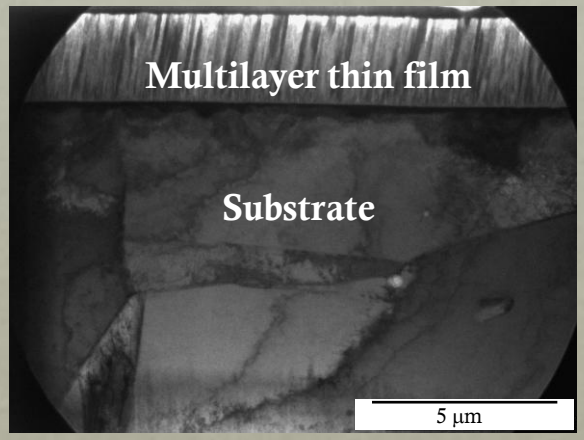


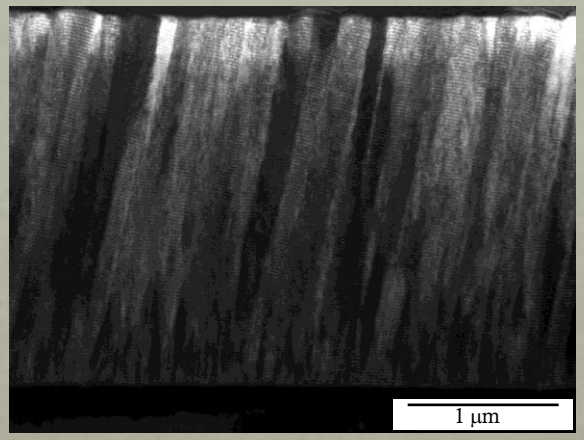
SEM

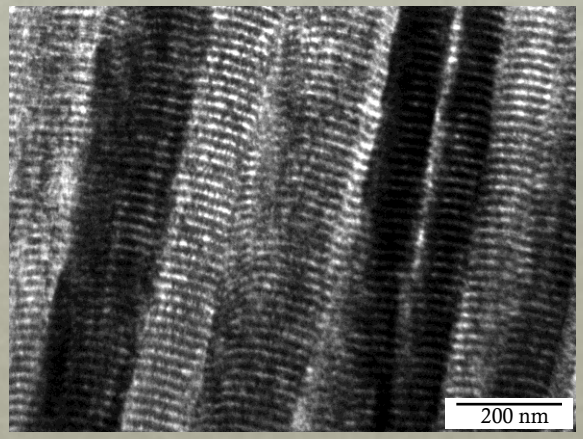
AS-DEPOSITED MULTILAYER THIN FILMS

FIB / TEM

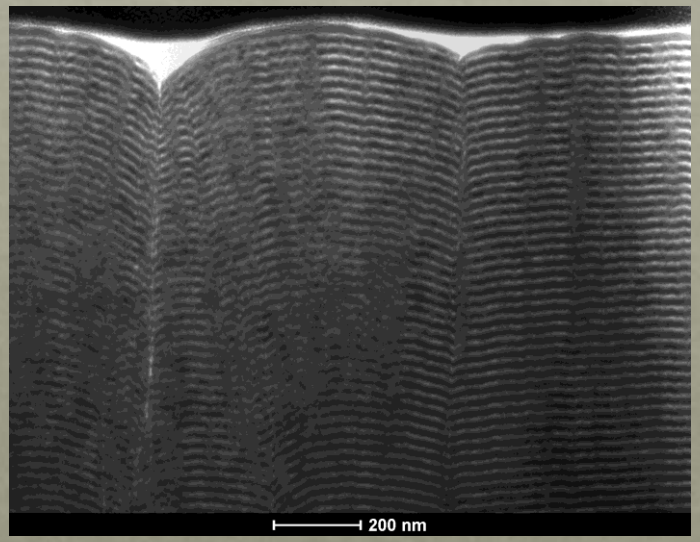
Ti/Al Λ = 20 nm



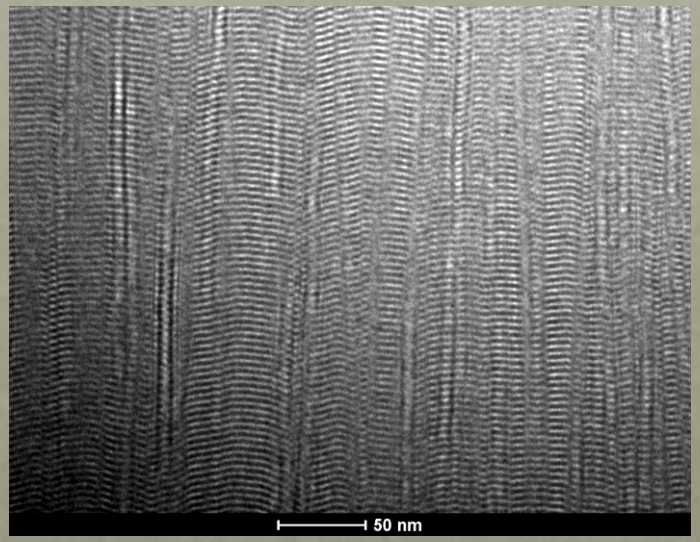




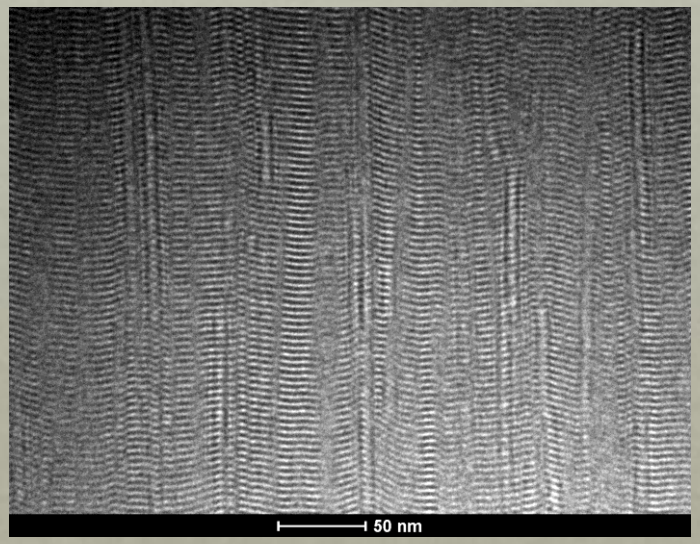
Ni/Ti Λ = 25 nm

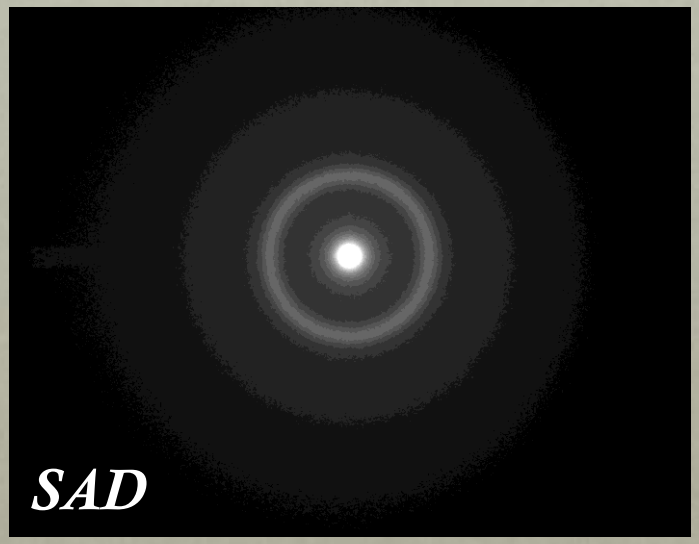


Ni/Ti Λ = 4 nm



AS-DEPOSITED MULTILAYER THIN FILMS

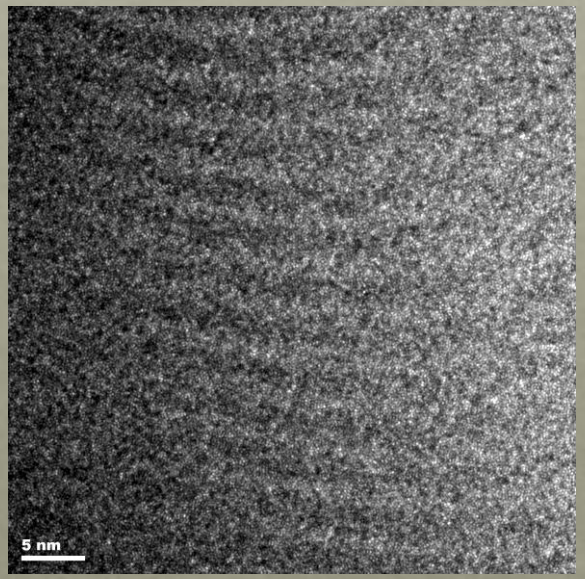


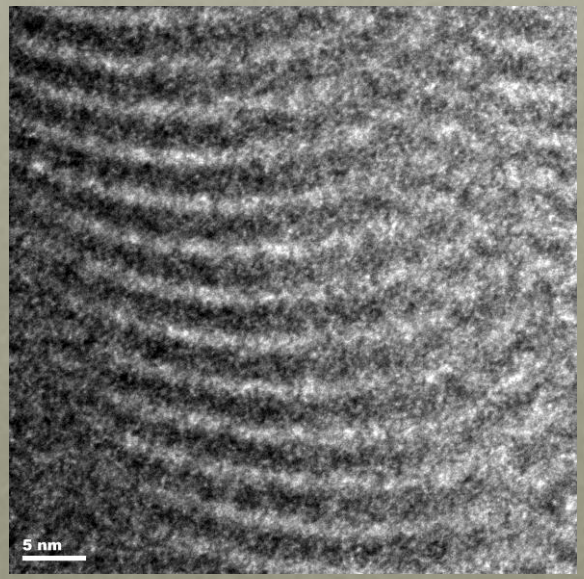


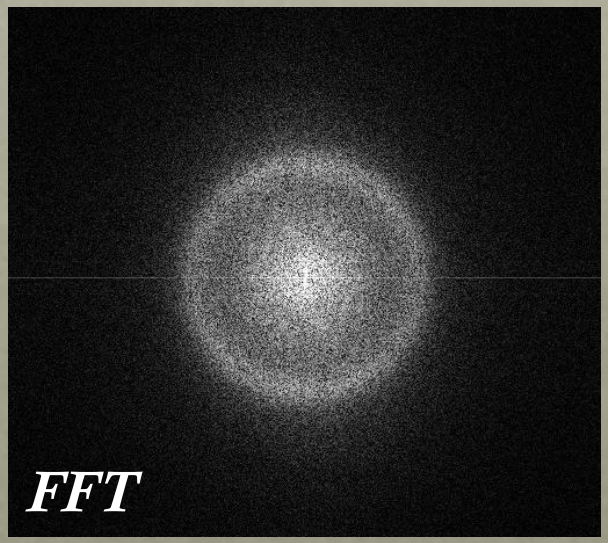
Ni/Ti Λ = 4 nm

FIB / TEM

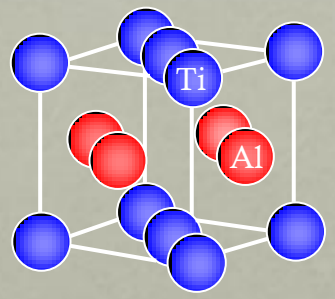
HREM



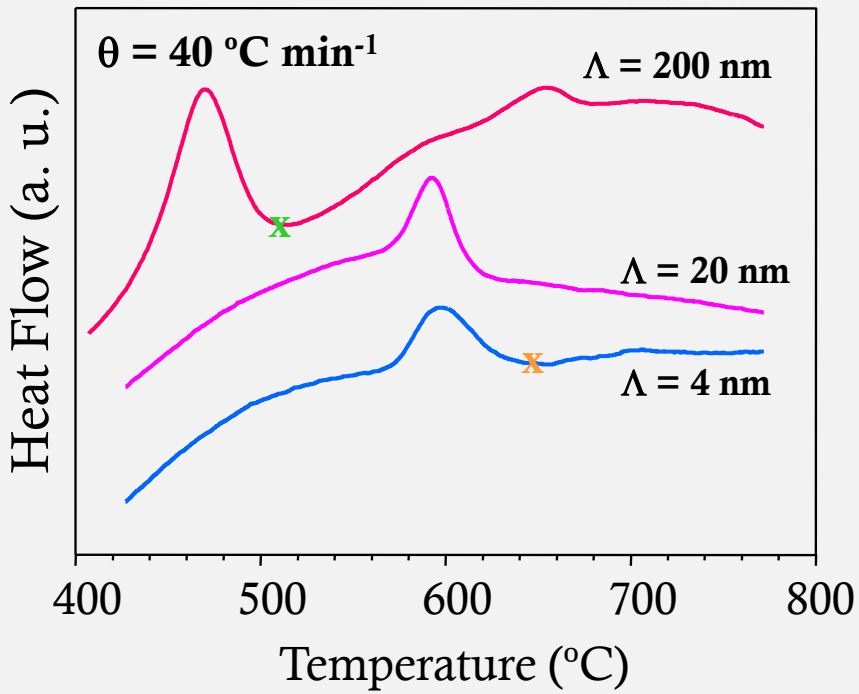


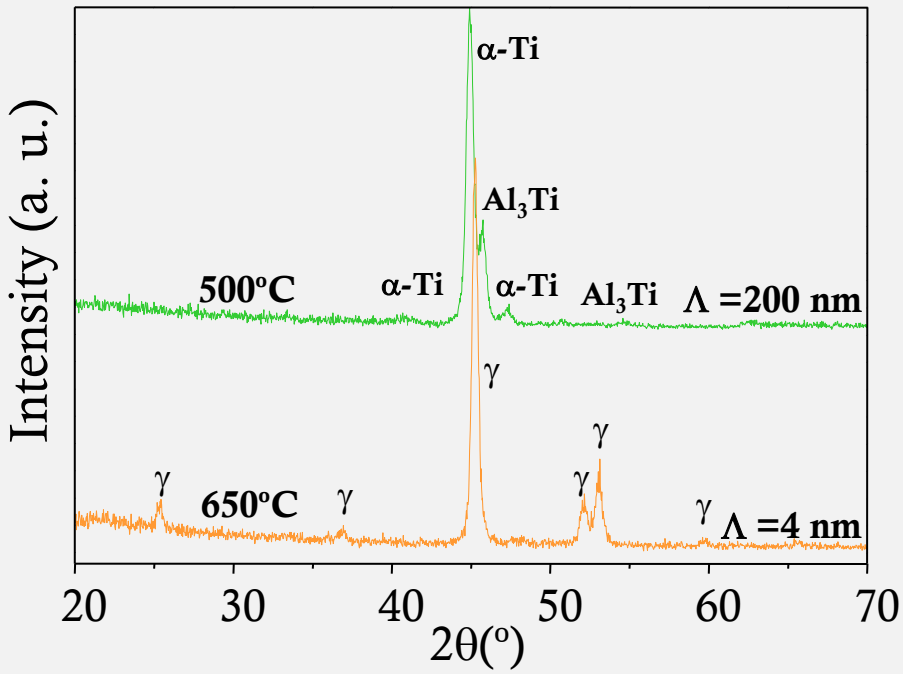


STRUCTURAL EVOLUTION



DSC

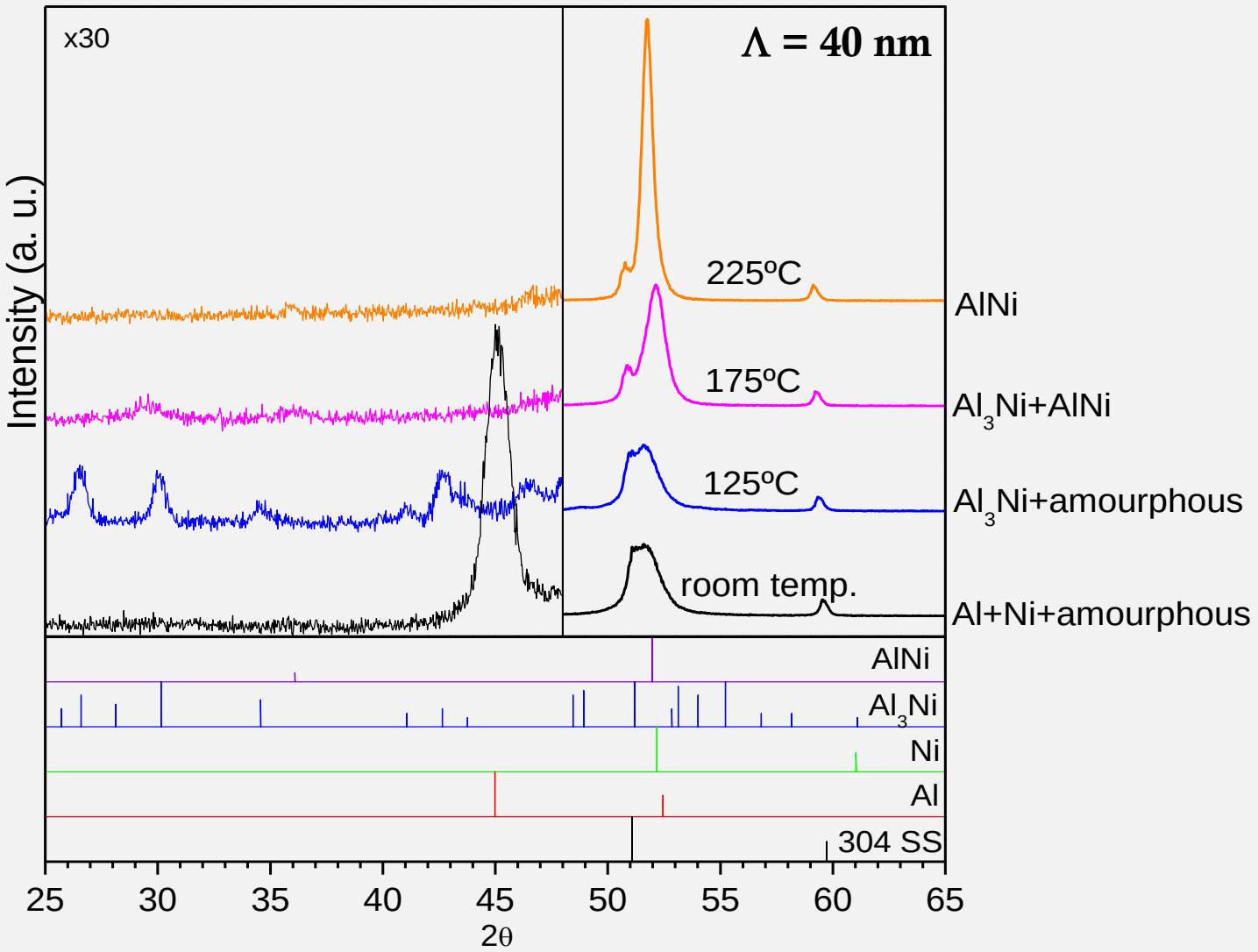




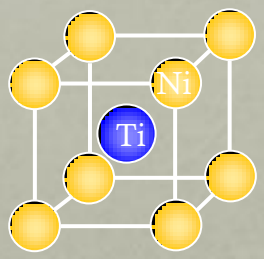
DSC sets performed up to 800°C combined with XRD measurements.

STRUCTURAL EVOLUTION

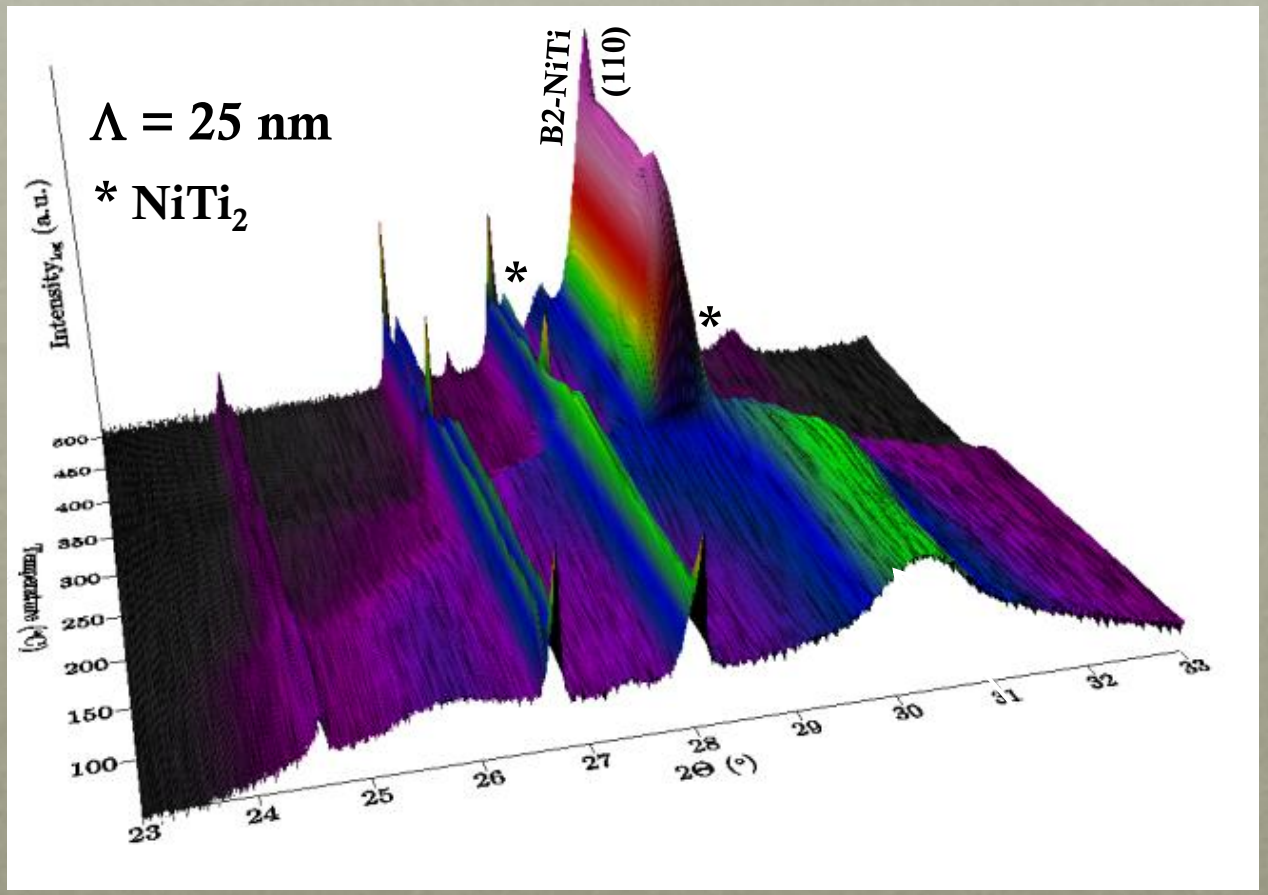
In situ High Temperature XRD ***Co radiation***



STRUCTURAL EVOLUTION



In situ High Temperature XRD ***Synchrotron radiation***



E = 11.5 keV

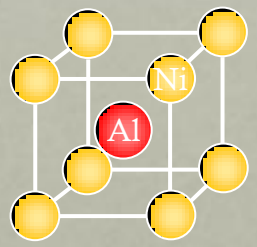
λ = 0.1078 nm

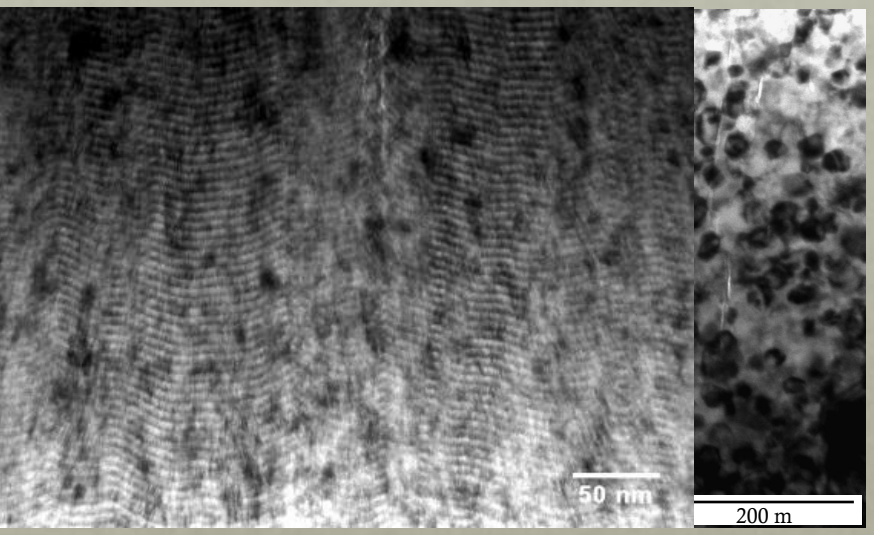
θ–2θ XRD with 25ºC steps

Substrate – Ti6Al4V

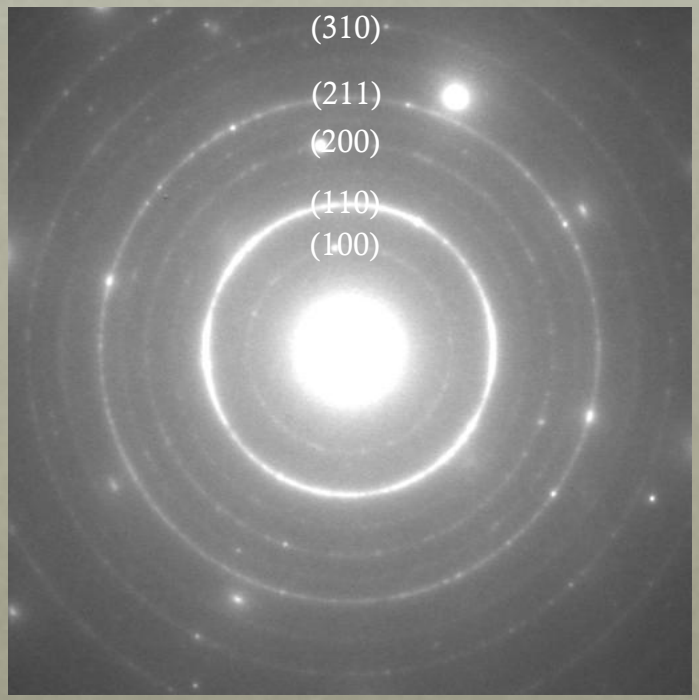
Heating rate – 60ºC/min

HEAT TREATED FILMS

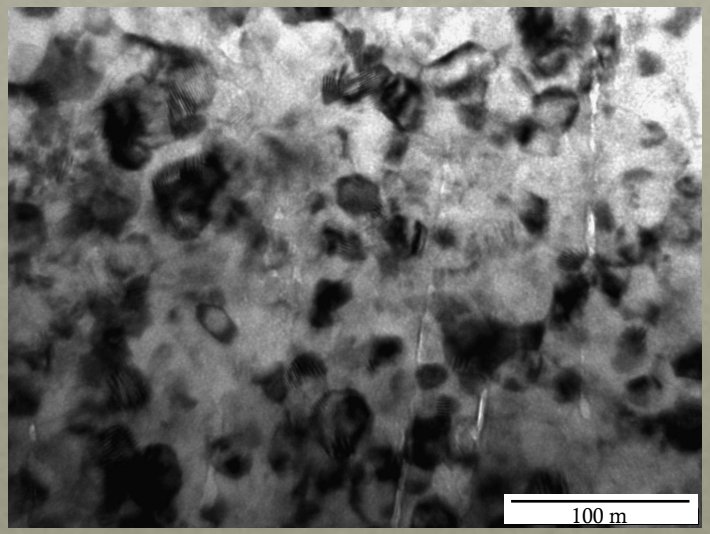




Λ= 5 nm 425ºC

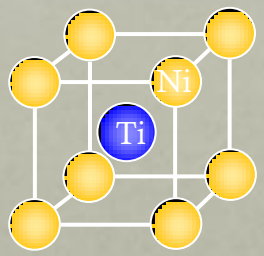


B2-NiAl (JSPDS card 44-1188)

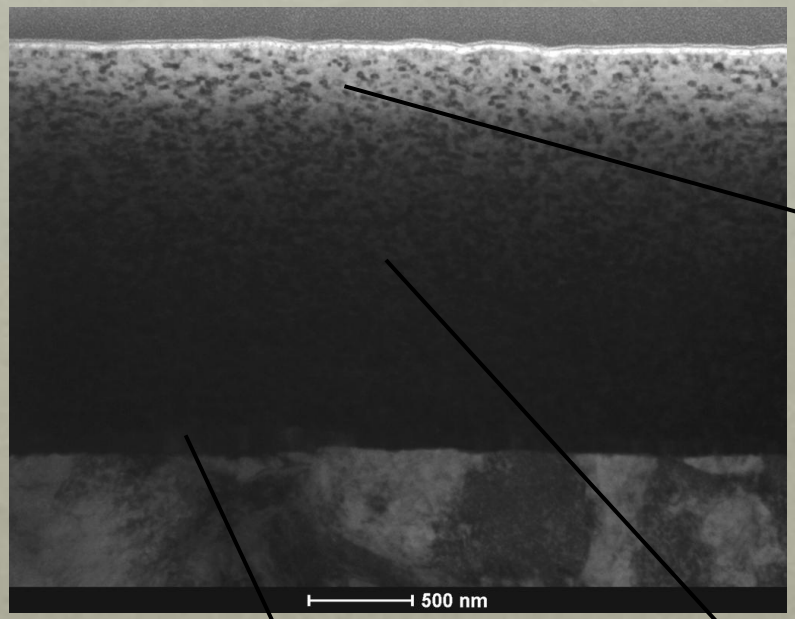


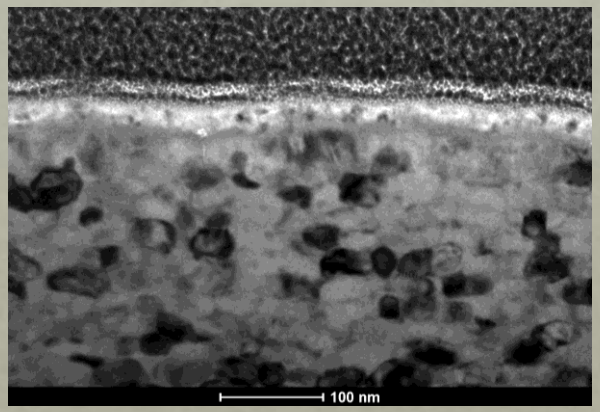
FIB / TEM

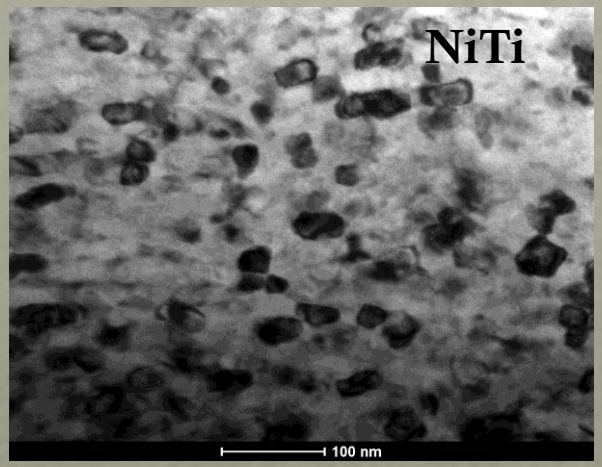
HEAT TREATED FILMS

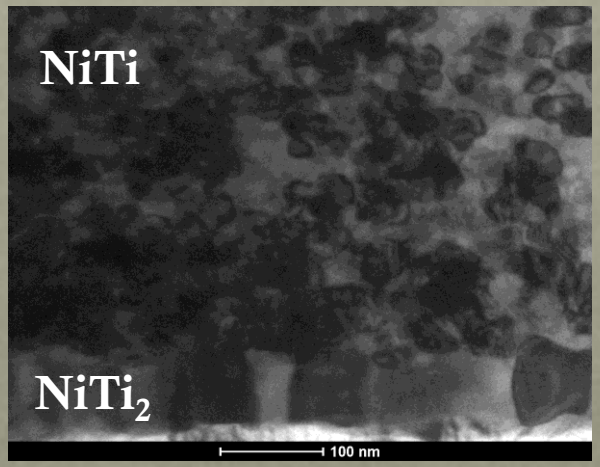


Λ = 25 nm



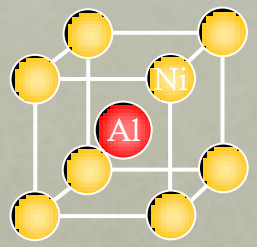






FIB / TEM

IGNITION TESTS



✓ Instantaneous reaction exhibiting a bright yellow flash

Ni/Al multilayer thin film with Λ = 40 nm and t_t > 3 μm.

✓ Self-propagation observed only in free-standing films, with modulation periods ≥ 14 nm.

APPLICATIONS: JOINING

Different approaches can be envisaged :

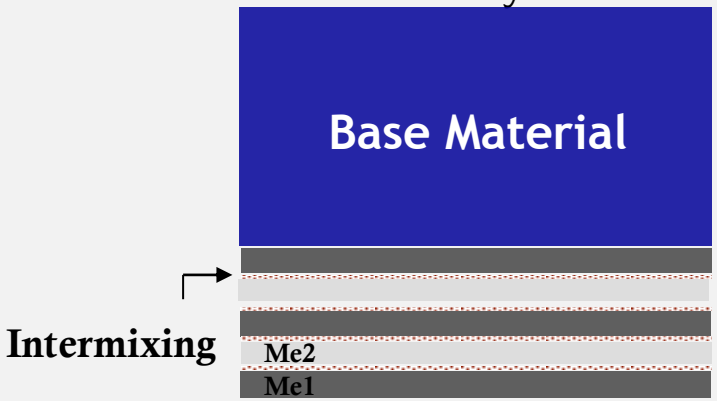
Reactive Brazing – reactive multilayers as heat sources suitable to melt the brazing alloy.

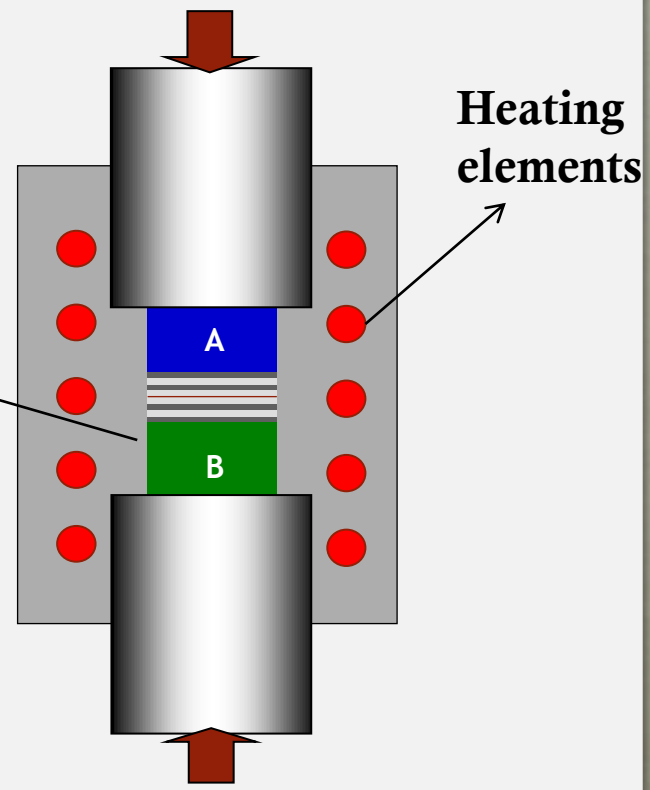
Reaction-Assisted Diffusion Bonding (RABD) – reactive multilayers enhance the diffusion bonding process by taking advantage of their improved diffusivity and reactivity.

Reactive Joining – exothermal reaction of the multilayers releases heat and promotes joining without requiring external heat sources or solder/braze alloys.

REACTION-ASSISTED DIFFUSION BONDING

Component coated with a reactive multilayer thin film





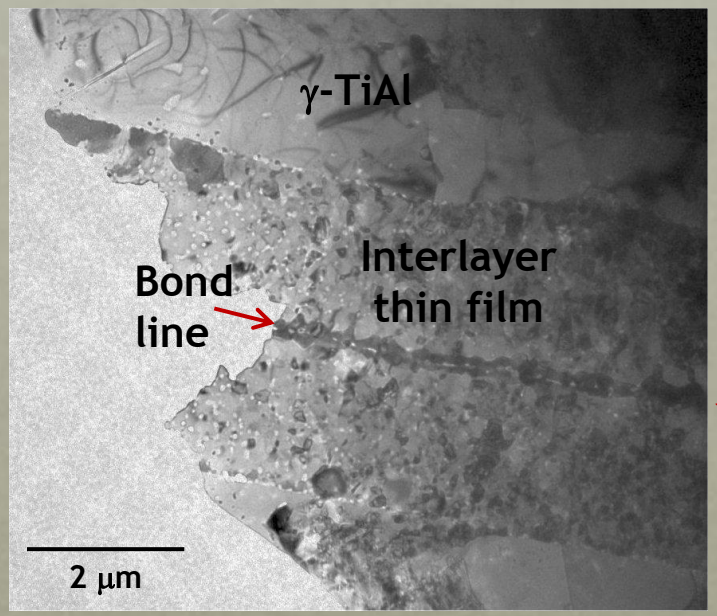
- Ti/Al multilayer thin films
- Ni/Al multilayer thin films
- Pd/Al multilayer thin films
- Ni/Ti multilayer thin films

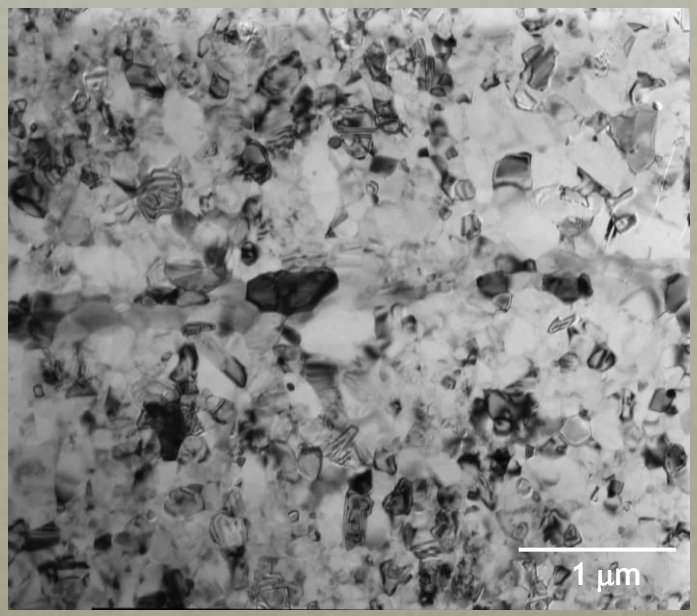
Reaction-assisted diffusion bonding - Reactive multilayer thin films (ML) with nanometric period are used as interlayer material.
ML films with nanometric modulation period (Λ) are directly deposited by magnetron sputtering onto the materials being joined.

RABD – Similar Joints

TiAl/TiAl
900ºC / 50 MPa / 1h
Ti/Al Λ = 4 nm

TEM

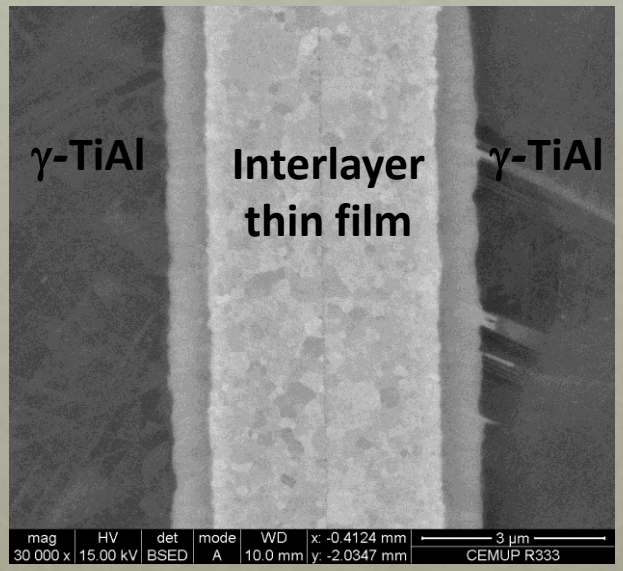




Bright-Field TEM images. The initial alternated layers of Ti and Al were replaced by nanocrystalline grains with sizes ranging from 50 to 300 nm.

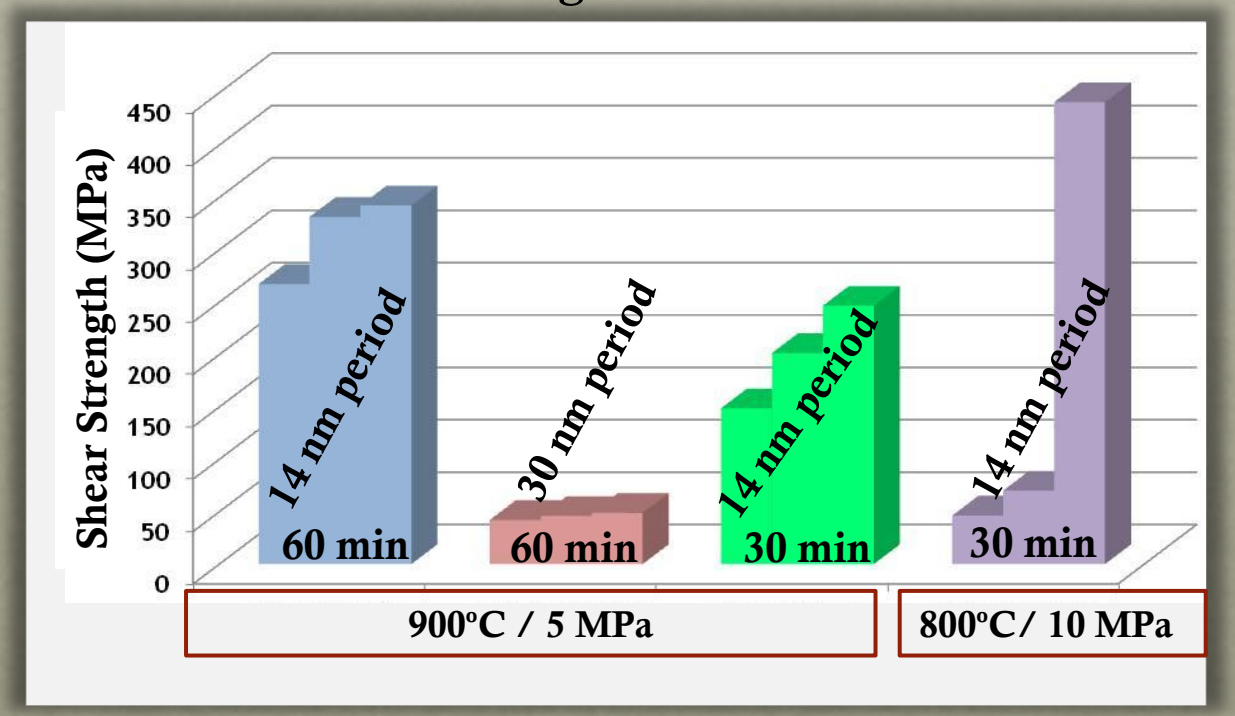
RABD – Similar Joints

TiAl/TiAl joints with Ni/Al interlayer



800ºC / 50 MPa / 1h
Ni/Al Λ = 14 nm

Shear Strength Test Results

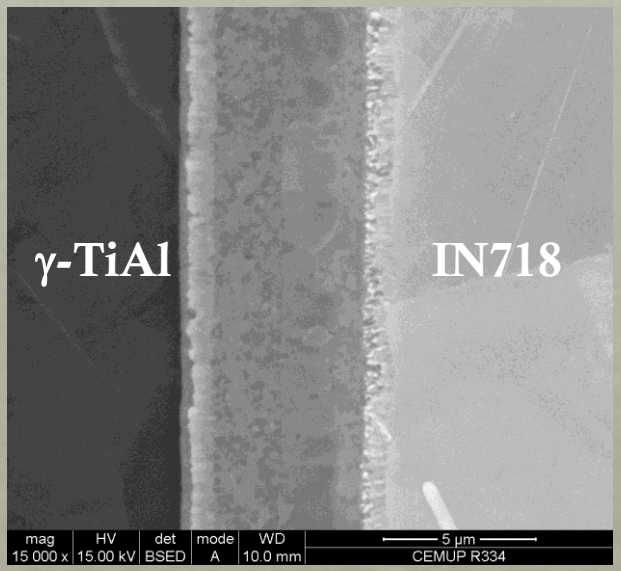


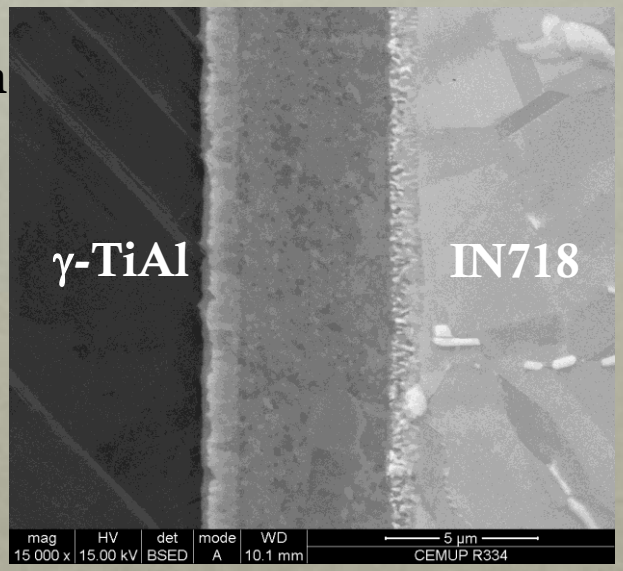
RABD – Dissimilar Joints

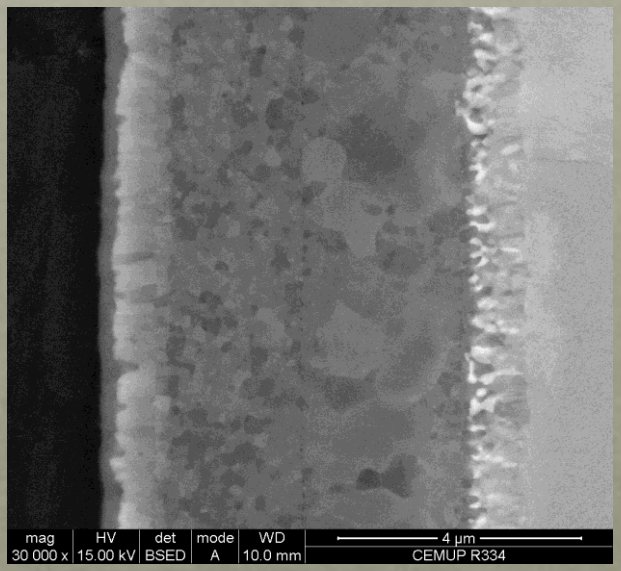
TiAl/Inconel

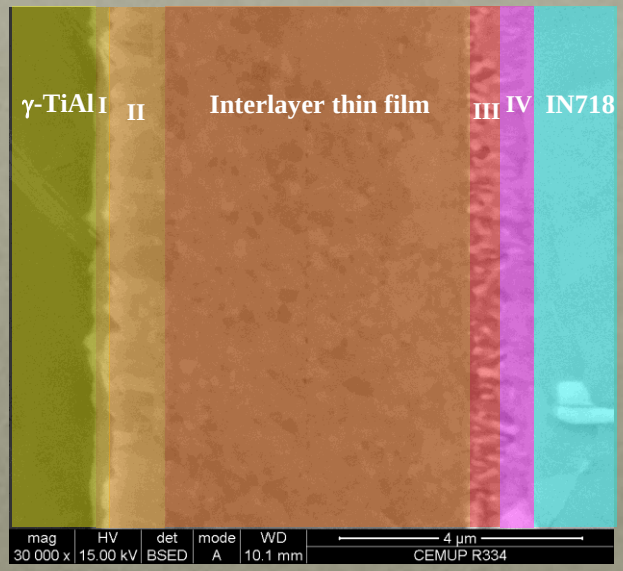
800ºC / 50 MPa / 1h

Ni/Al Λ = 14 nm





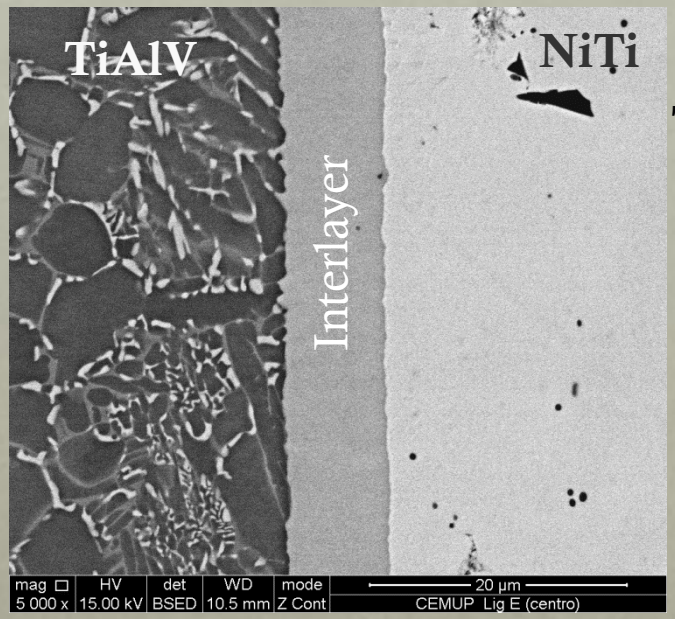


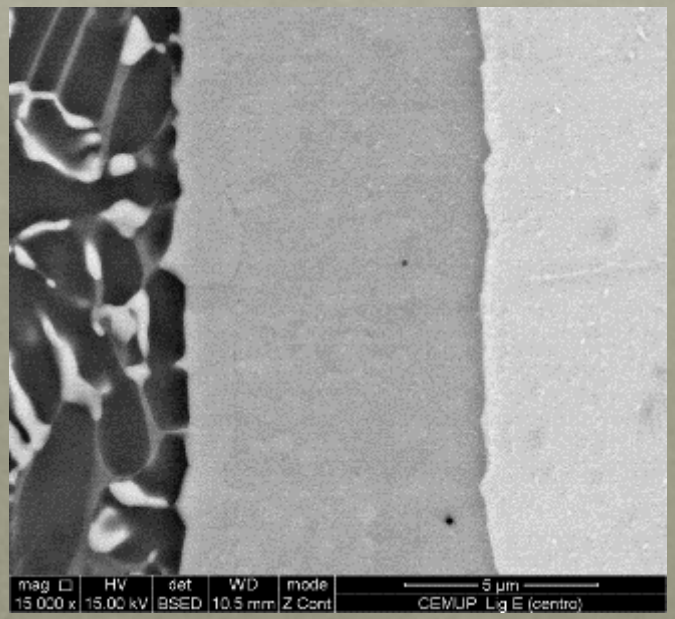


RABD – Dissimilar Joints

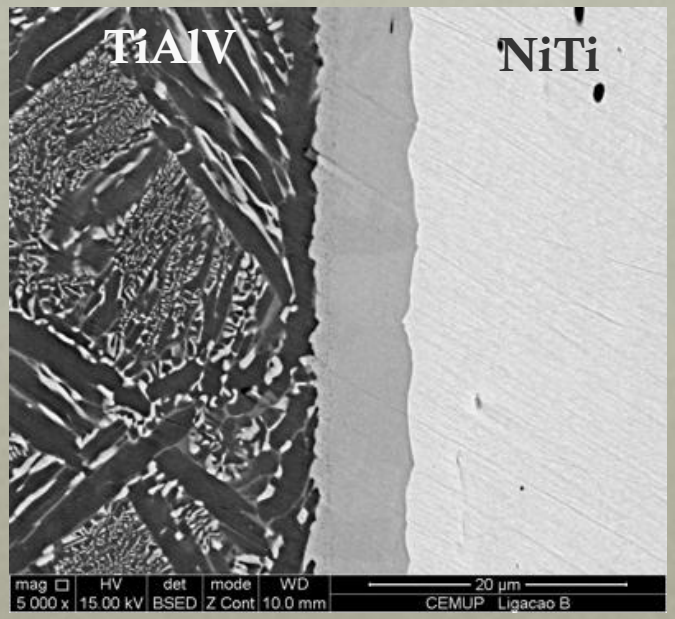
TiAlV/NiTi

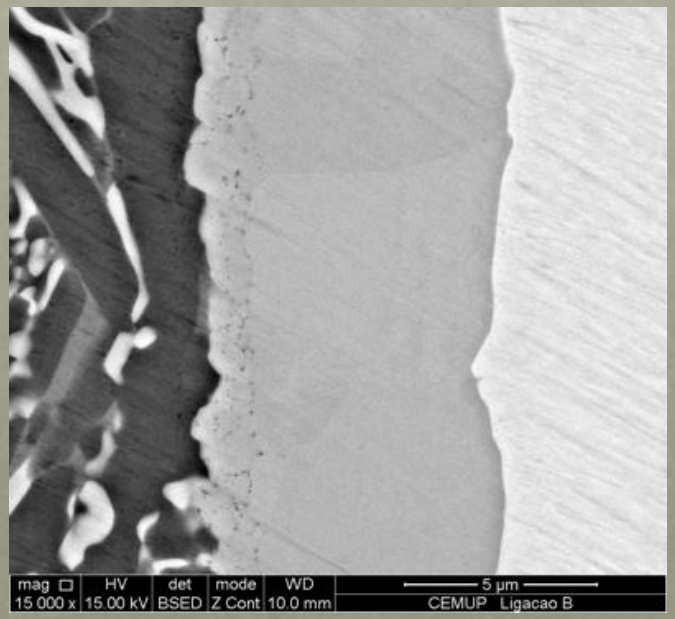
850°C / 5 MPa / 1h
Ni/Ti Λ = 25 nm





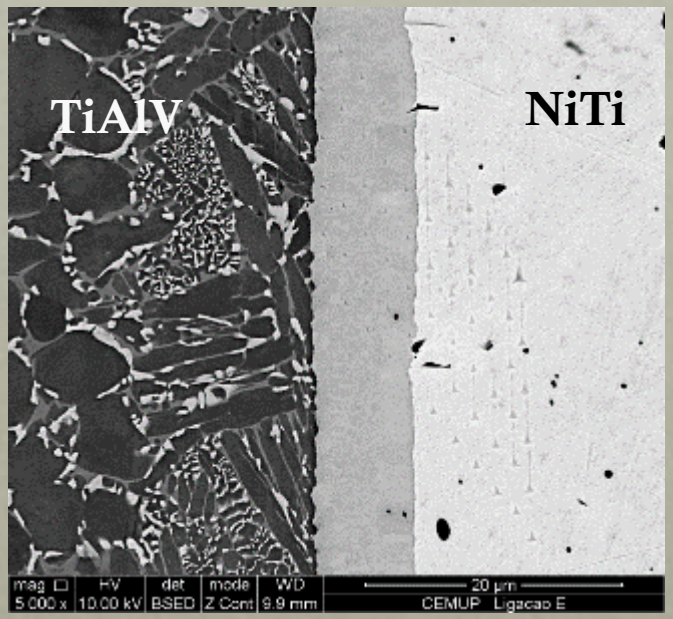
900°C / 5 MPa / 1h
Ni/Ti Λ = 12 nm

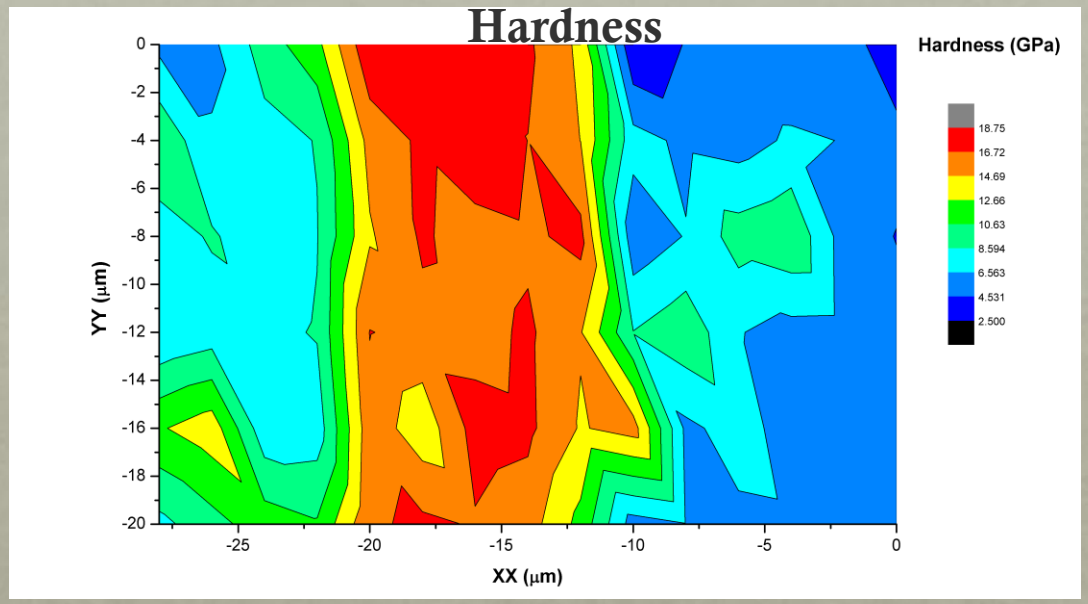


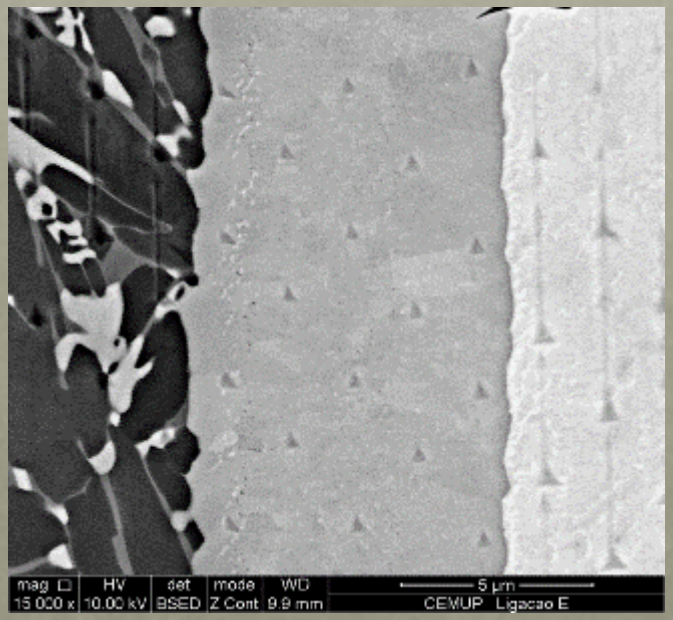


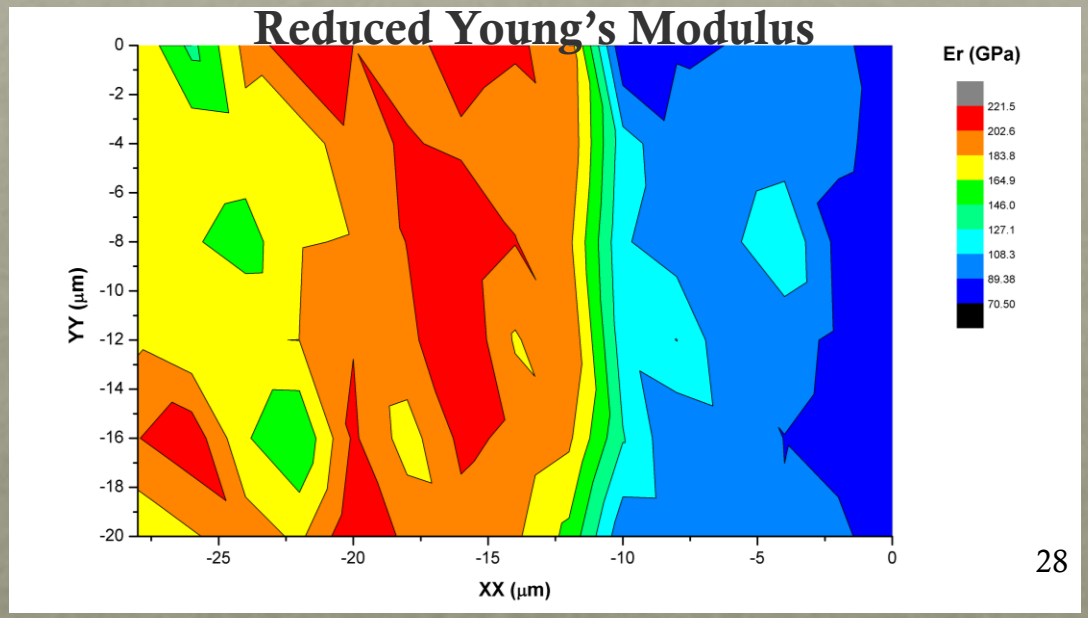
RABD – Dissimilar Joints

TiAlV/NiTi 850ºC / 5 MPa / 1h Ni/Ti Λ = 25 nm



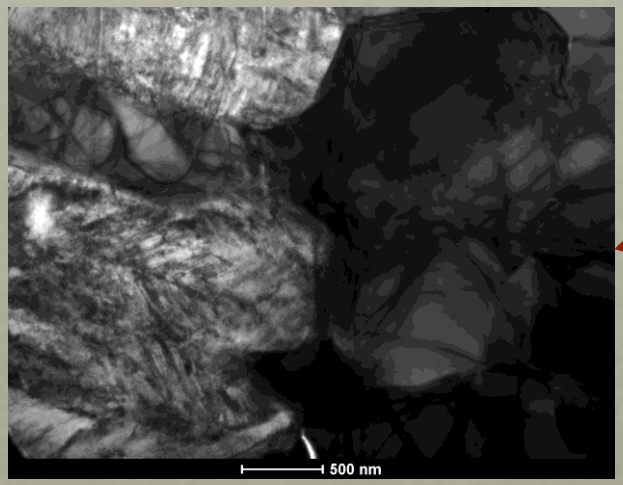


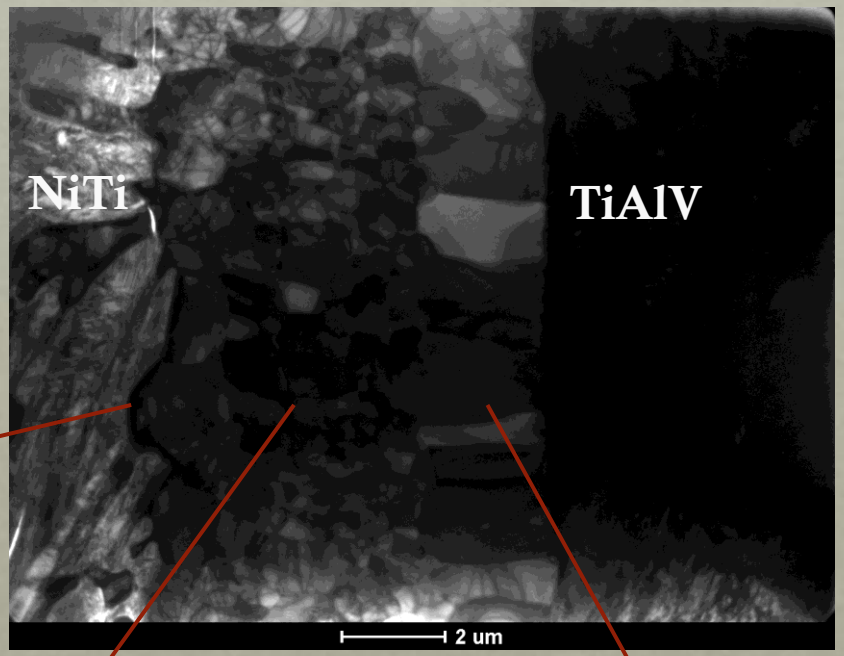


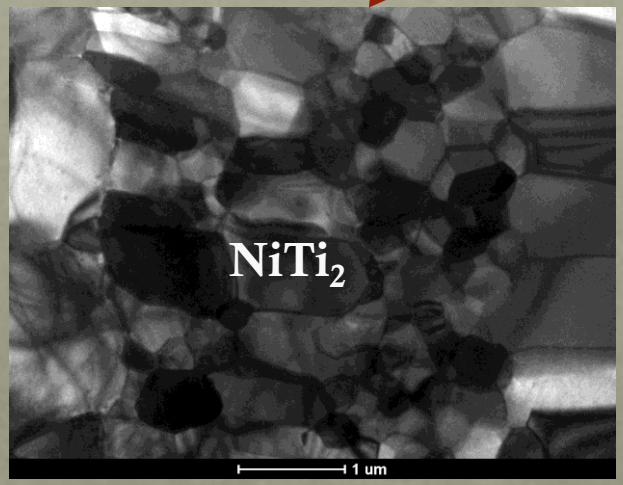


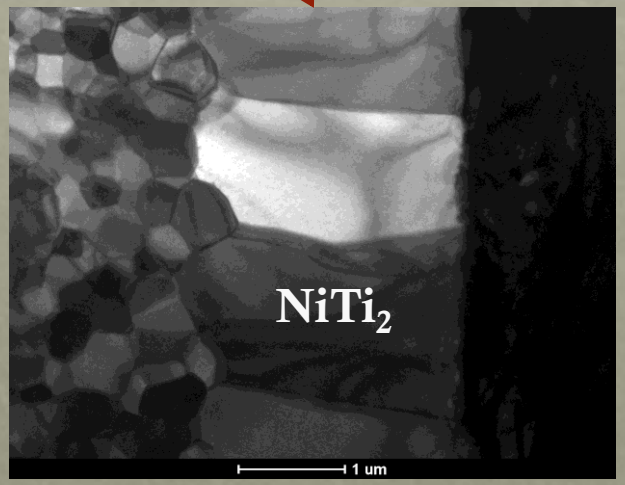
RABD – Dissimilar Joints

TiAlV/NiTi
850ºC / 5 MPa / 1h
Ni/Ti Λ = 25 nm





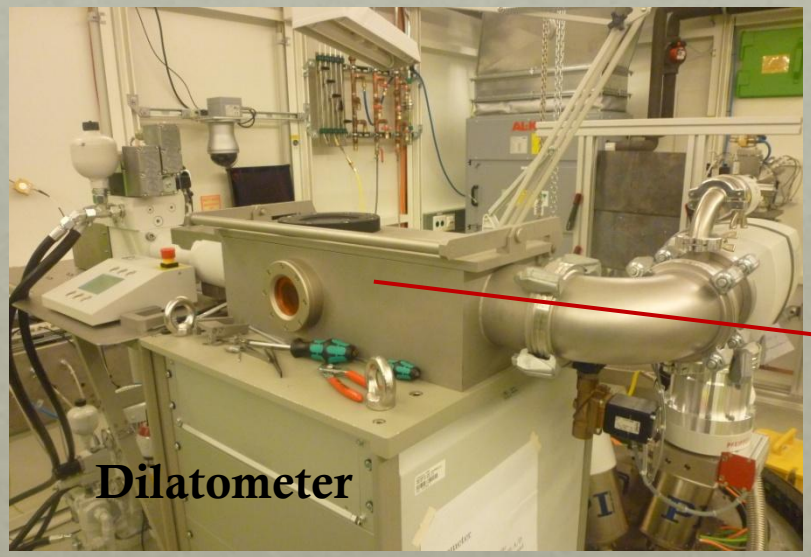


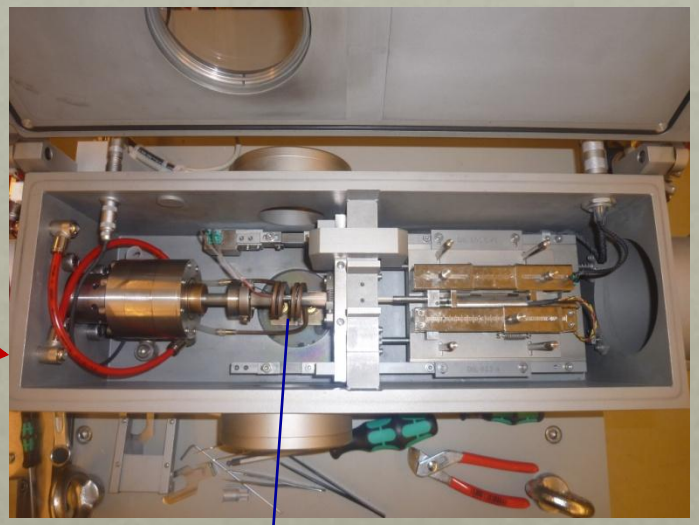


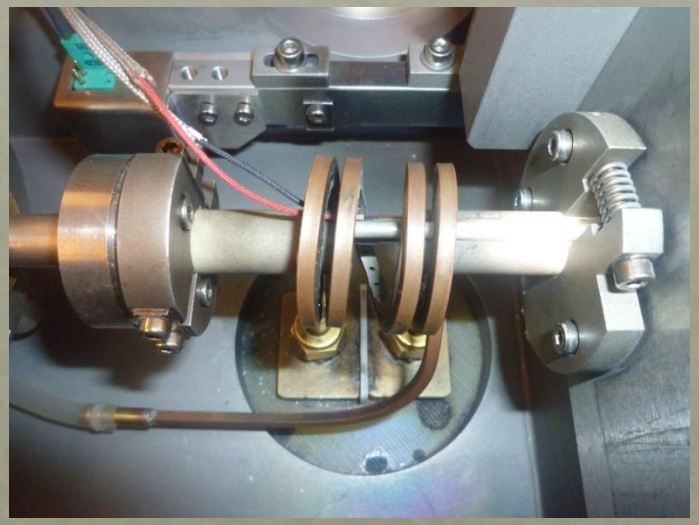
FIB / TEM

RABD – Dissimilar Joints

P07 The High Energy Materials Science Beamline



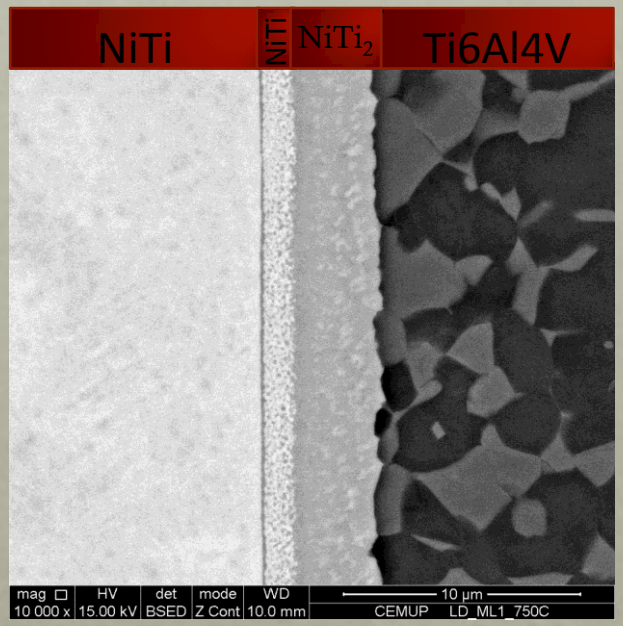




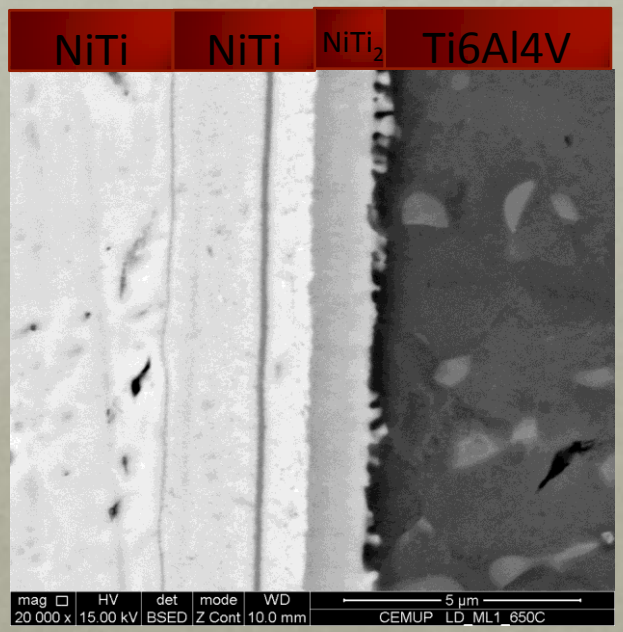
RABD – Dissimilar Joints

10 MPa
30 min

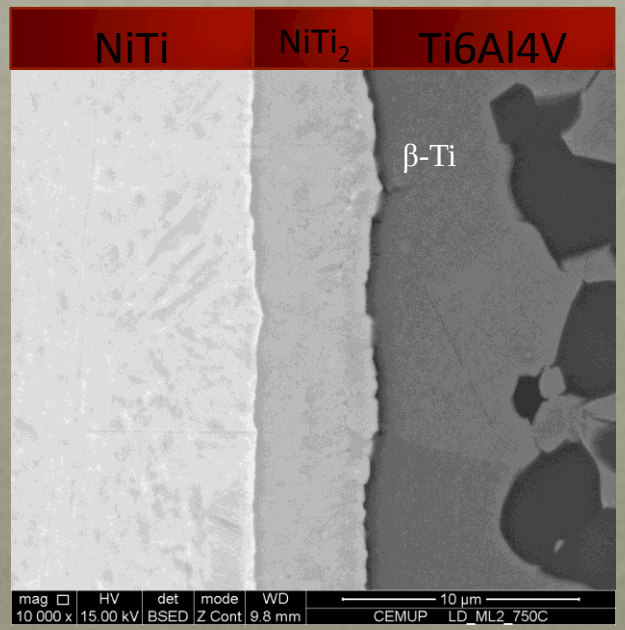
Ni/Ti Λ = 12 nm @ 750°C



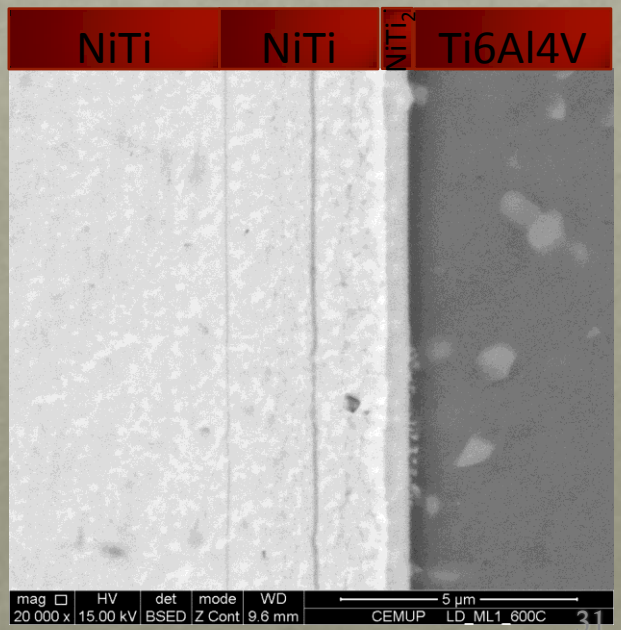
Ni/Ti Λ = 12 nm @ 650°C



Ni/Ti Λ = 25 nm @ 750°C

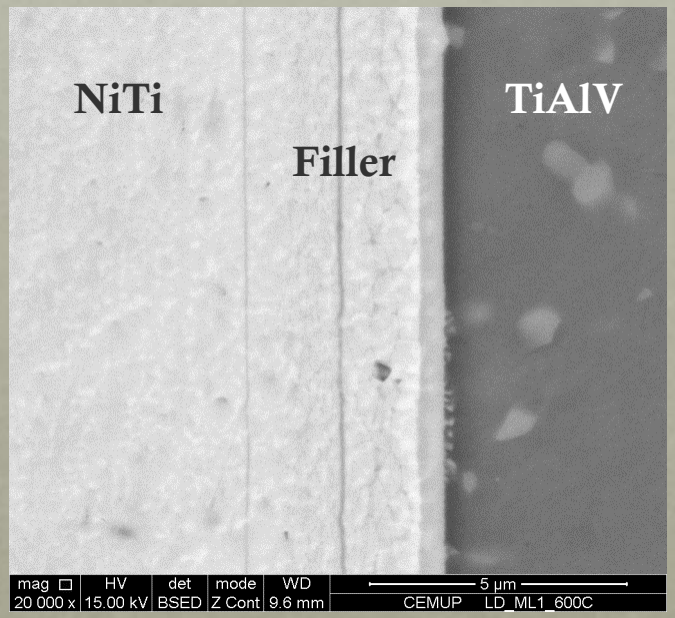


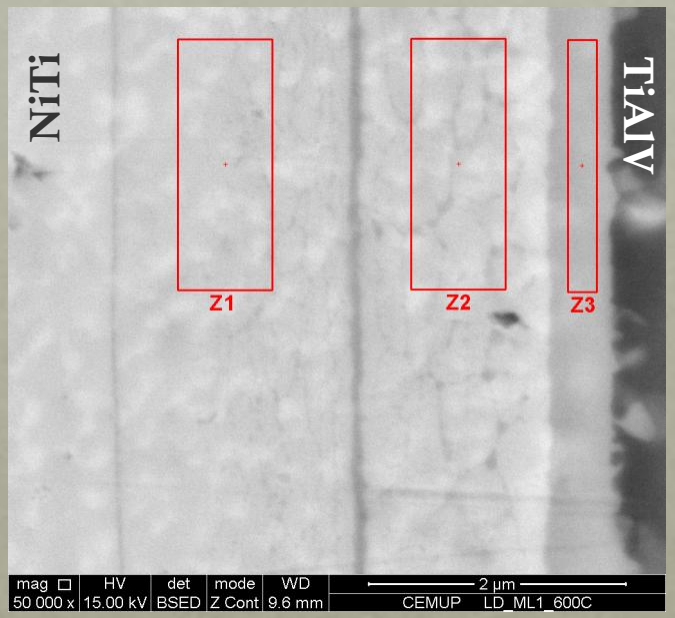
Ni/Ti Λ = 12 nm @ 600°C



RABD – Dissimilar Joints

TiAlV/NiTi **600ºC / 10 MPa / 30min** **Ni/Ti Λ = 12 nm**



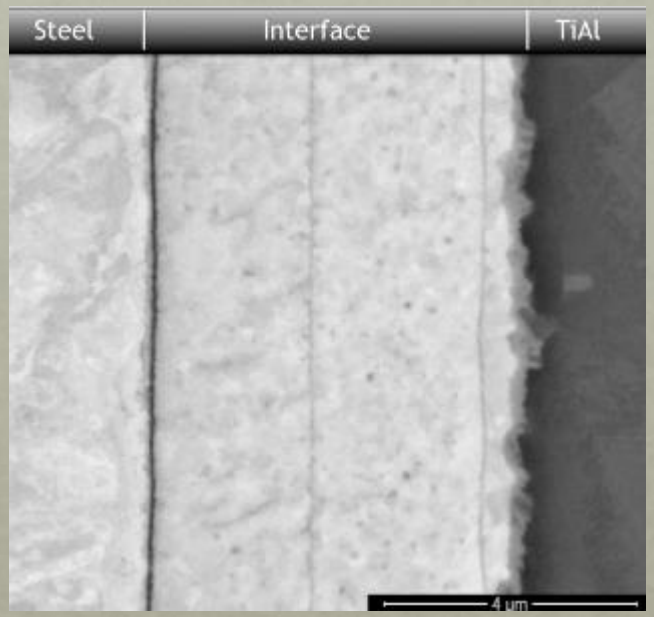


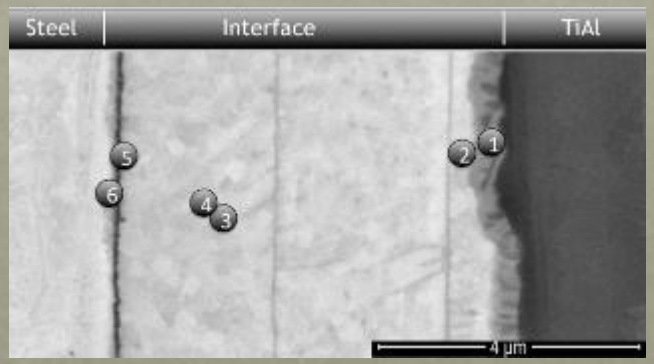
Zone 1	% at.
Ti	50.8
Ni	49.2

Zone 2	% at.
Ti	52.0
Ni	48.0

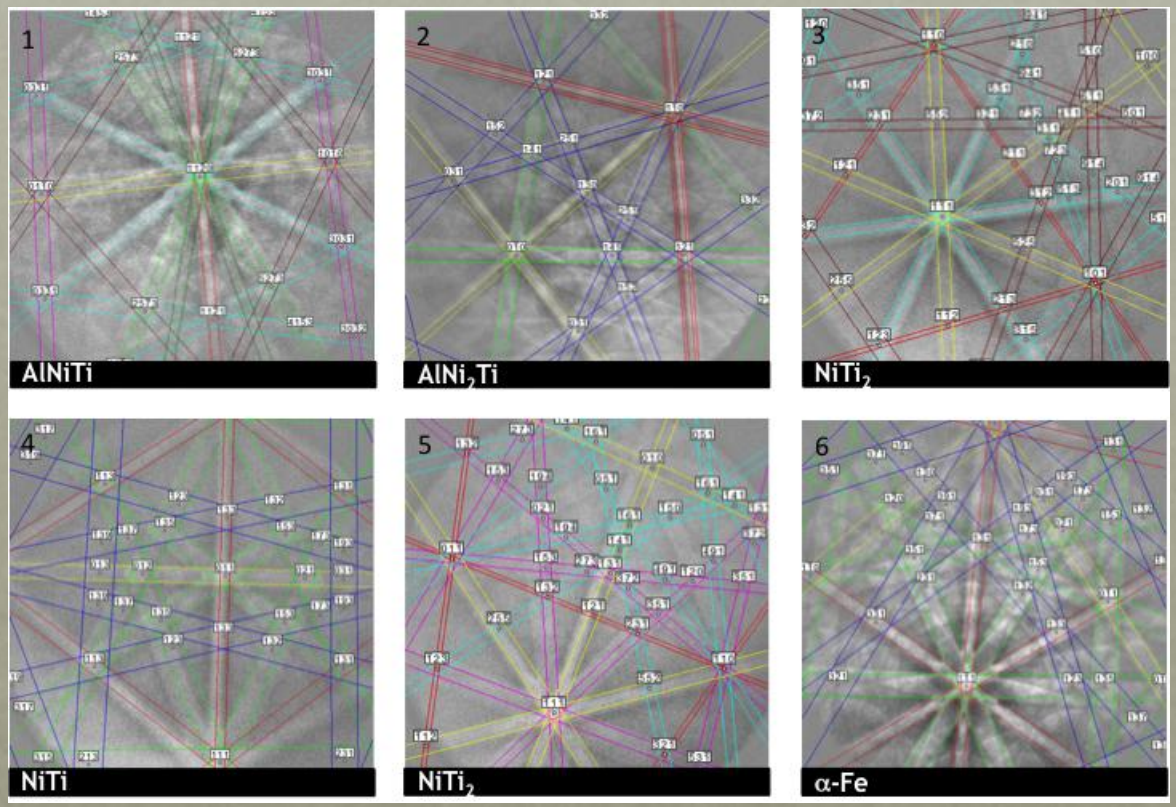
Zone 3	% at.
Ti	60.0
Ni	37.2
Al	2.8

RABD – Dissimilar Joints





TiAl/Steel
800ºC / 10 MPa / 30min
Ni/Ti Λ = 30 nm



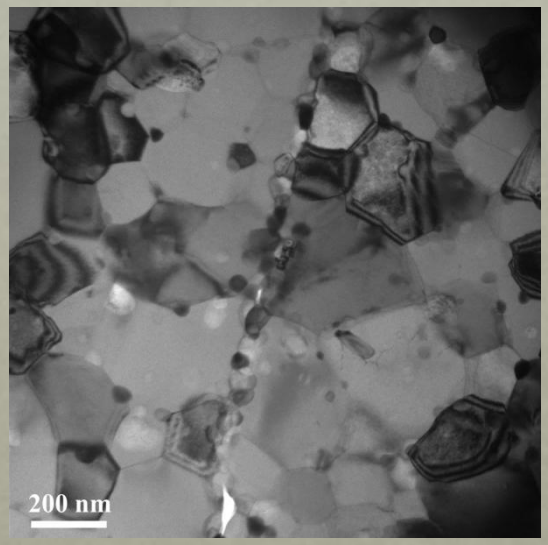
EBSD Kikuchi pattern indexation

RABD – Dissimilar Joints

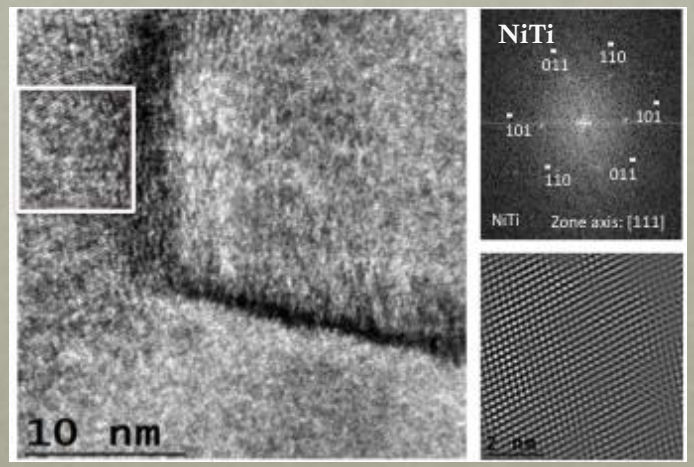
FIB / TEM

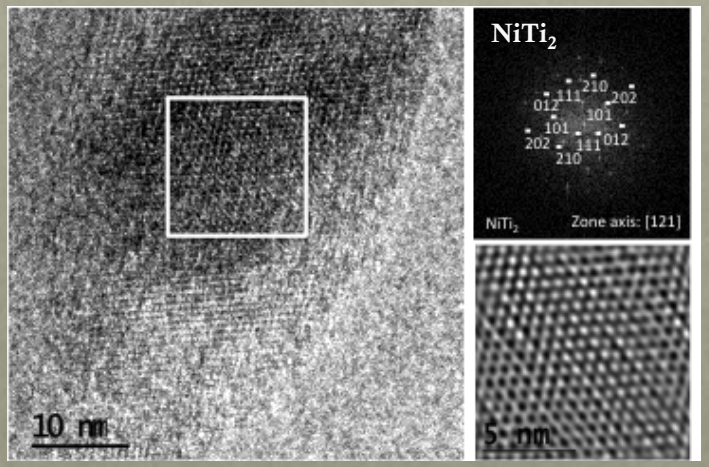
TiAl/Steel

800ºC / 10 MPa / 60min
Ni/Ti Λ = 30 nm



Bond-line





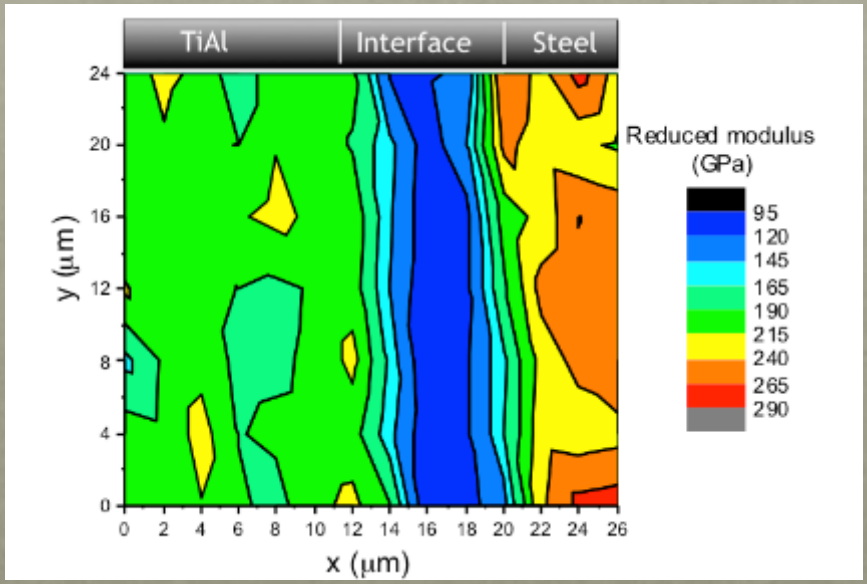
HREM / FFT

RABD – Dissimilar Joints

Period (nm)	Bonding conditions (temperature/time/pressure)	Average Shear Strength (MPa)
30	700 °C / 60 min / 50 MPa	54
30	800 °C / 60 min / 10 MPa	**225**
60	800 °C / 60 min / 10 MPa	83

Shear Strength TiAl/Steel joints Ni/Ti interlayer

TiAl/Steel
800ºC / 10 MPa / 60min
Ni/Ti Λ = 30 nm



SUMMARY

Reactive nanoscale multilayers undergo interdiffusion and mixing in an exothermic (and self-propagating) reaction, releasing energy. Therefore, they show potential as localized heat sources for joining applications.

Using these energetic materials, **reaction-assisted diffusion bonding** has been successfully carried out for dissimilar joining of different materials

Sound joints were achieved at less demanding conditions (temperature, pressure or time)

ACKNOWLEDGMENTS

FEDER funds through the program COMPETE – Programa Operacional Factores de Competitividade, and National funds through FCT – Fundação para a Ciência e a Tecnologia , under project UID/EMS/00285/2013, and the grant SFRH/BPD/109788/2015.

We acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation facilities and we would like to thank Dr. Baehtz for assistance in using beamline BM20– Proposal MA-1637– "*In-situ phase evolution of sputtered reactive multilayers*"

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