Symposium of World Experts in Diffusion Bonding (WEDB)

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Can you see the bond-line?

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

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

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.

self-propagating reaction in a multilayer system after ignition

Direction of the self-propagating reaction

Alloy AB

Reaction zone

Unreacted layers

Nanoscale material film A

Nanoscale material film B

Bilayer thickness

Intermixing

Ignition

ECS Transactions 33 (2010) 307
**REACTIVE MULTILAYERS – DEPOSITION TECHNIQUE**

- DC magnetron sputtering
- High purity $\text{Me}_1$ and $\text{Me}_2$ targets
- Base pressure $< 5 \times 10^{-4}$ Pa
- $P = 0.3 – 0.4$ Pa
- Substrate bias = -40 V
- Total thickness $\approx 2.5$ µm
- Periods ($\Lambda$) between 4 and 200 nm

\[
\Lambda = \frac{t}{d \cdot rp}
\]

$t$ – 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

Ti/Al $\Lambda = 200$ nm

Ni/Al $\Lambda = 140$ nm

Pd/Al $\Lambda = 25$ nm

Ni/Ti $\Lambda = 70$ nm
Multilayer thin film

Substrate

AS-DEPOSITED MULTILAYER THIN FILMS

Ti/Al $\Lambda = 20 \text{ nm}$

Ni/Ti $\Lambda = 25 \text{ nm}$

Ni/Ti $\Lambda = 4 \text{ nm}$
AS-DEPOSITED MULTILAYER THIN FILMS

Ni/Ti $\Lambda = 4$ nm

HREM

SAD

FIB / TEM

FFT
DSC

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

In situ High Temperature XRD Co radiation

AlNi
Al$_3$Ni+AlNi
Al$_3$Ni+amourphous
Al+Ni+amourphous

Intensity (a. u.)

225ºC
175ºC
125ºC
room temp.

$\Lambda = 40 \text{ nm}$

25 30 35 40 45 50 55 60 65
In situ High Temperature XRD  Synchrotron radiation

$E = 11.5$ keV
$\lambda = 0.1078$ nm
$\theta$–$2\theta$ XRD with 25°C steps
Substrate – Ti6Al4V
Heating rate – 60°C/min

$\Lambda = 25$ nm
$\ast$ NiTi$_2$

B2-NiTi (110)
HEAT TREATED FILMS

\[ \Lambda = 5 \text{ nm} \quad 425^\circ\text{C} \]

B2-NiAl (JSPDS card 44-1188)

FIB / TEM
HEAT TREATED FILMS

$\Lambda = 25 \text{ nm}$

NiTi$_2$

NiTi
IGNITION TESTS

- Instantaneous reaction exhibiting a bright yellow flash

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

- Self-propagation observed only in free-standing films, with modulation periods $\geq 14$ nm.
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** - 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.
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

800°C / 50 MPa / 1h
Ni/Al Λ = 14 nm

Shear Strength Test Results

Shear Strength (MPa)

900°C / 5 MPa
800°C / 10 MPa
RABD – Dissimilar Joints

TiAl/Inconel
800°C / 50 MPa / 1h
Ni/Al $\Lambda = 14$ nm
RABD – Dissimilar Joints

850°C / 5 MPa / 1h Ni/Ti A = 25 nm

900°C / 5 MPa / 1h Ni/Ti A = 12 nm
RABD – Dissimilar Joints

TiAlV/NiTi

850°C / 5 MPa / 1h Ni/Ti \( \Lambda = 25 \text{ nm} \)

![Image of TiAlV/NiTi joint](image1)

**Hardness**

![Hardness graph](image2)

**Reduced Young’s Modulus**

![Reduced Young’s Modulus graph](image3)
**RABD – Dissimilar Joints**

**TiAlV/NiTi**
850°C / 5 MPa / 1h
Ni/Ti $\Lambda = 25$ nm

**FIB / TEM**
RABD – Dissimilar Joints

P07 The High Energy Materials Science Beamline

Dilatometer

NiTi/TiAlV Joint
RABD – Dissimilar Joints

Ni/Ti  λ = 12 nm @ 750°C

Ni/Ti  λ = 25 nm @ 750°C

10 MPa
30 min

Ni/Ti  λ = 12 nm @ 650°C

Ni/Ti  λ = 12 nm @ 600°C

β-Ti
RABD – Dissimilar Joints

TiAlV/NiTi  
600°C / 10 MPa / 30min  
Ni/Ti  $\Lambda = 12$ nm

<table>
<thead>
<tr>
<th>Zone 1</th>
<th>% at.</th>
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<tbody>
<tr>
<td>Ti</td>
<td>50.8</td>
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<tr>
<td>Ni</td>
<td>49.2</td>
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<tr>
<td>Ti</td>
<td>52.0</td>
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<tr>
<td>Ni</td>
<td>48.0</td>
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<td>Al</td>
<td>2.8</td>
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<th>% at.</th>
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<tr>
<td>Ti</td>
<td>60.0</td>
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<tr>
<td>Ni</td>
<td>37.2</td>
</tr>
<tr>
<td>Al</td>
<td>2.8</td>
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</table>
RABD – Dissimilar Joints

TiAl/Steel
800°C / 10 MPa / 30min
Ni/Ti $\Lambda = 30 \text{ nm}$

EBSD Kikuchi pattern indexation
RABD – Dissimilar Joints

**FIB / TEM**

TiAl/Steel

800°C / 10 MPa / 60min

Ni/Ti \( \Lambda = 30 \text{ nm} \)

**HREM / FFT**
# RABD – Dissimilar Joints

<table>
<thead>
<tr>
<th>Period (nm)</th>
<th>Bonding conditions (temperature/time/pressure)</th>
<th>Average Shear Strength (MPa)</th>
<th>Shear Strength TiAl/Steel joints Ni/Ti interlayer</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>700 °C / 60 min / 50 MPa</td>
<td>54</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>800 °C / 60 min / 10 MPa</td>
<td>225</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>800 °C / 60 min / 10 MPa</td>
<td>83</td>
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TiAl/Steel
800°C / 10 MPa / 60min
Ni/Ti  $\Lambda = 30$ nm
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).
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