



Empa

Materials Science and Technology

Nano-Joining Technologies

Dr. Pierangelo Gröning

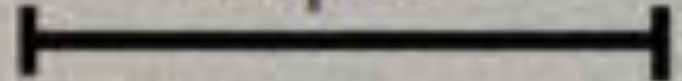
Trends in Mikro Nano

Swiss Micro- & Nanotechnology Network

Basel, 30. November 2017

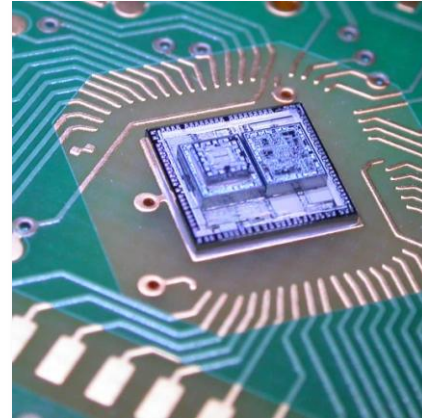
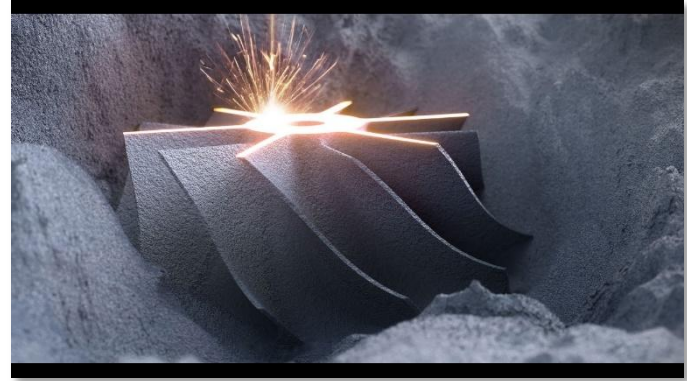
pierangelo.groening@empa.ch

30µm

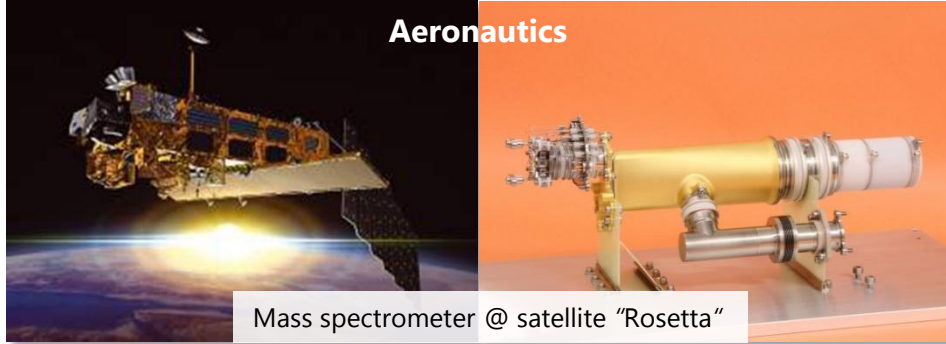


Joining Technologies

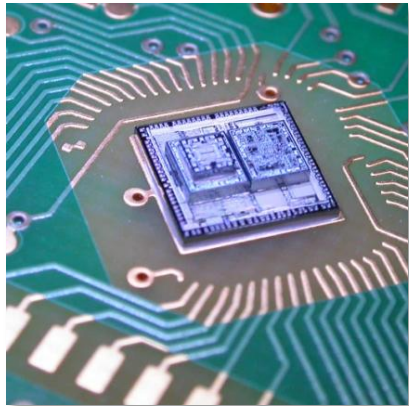
Barely a Device without Joining Processes



Brazing & Soldering Applications @ Empa



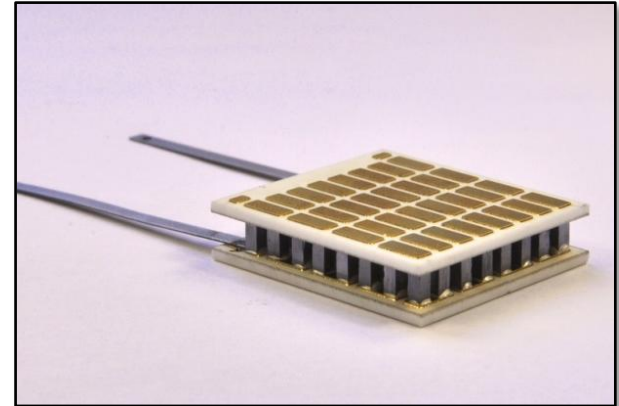
Microelectronics & Sensors



Turbines

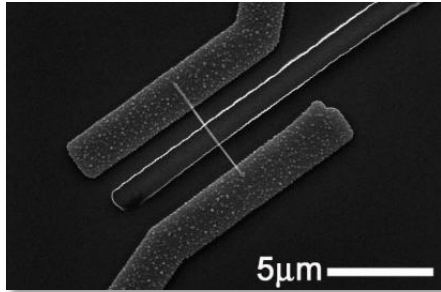


Thermoelectric



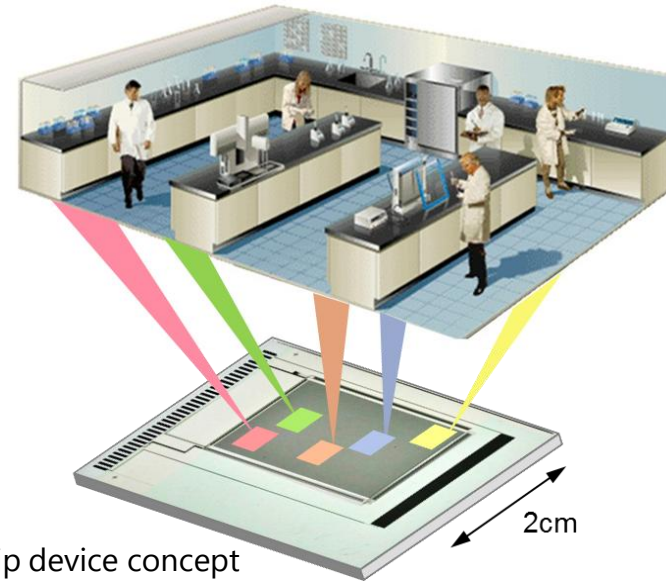
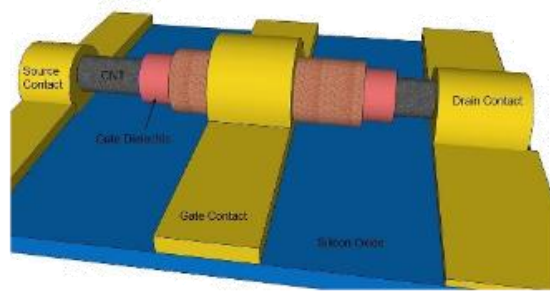
Advanced bonding & packaging technologies require

- ✓ Low- T , pressure-less, solvent-free joining process with high alignment accuracy
- ✓ Hybrid nanotechnology (i.e. bonding of wide variety of dissimilar materials)
- ✓ Heterogenous integration (i.e. combine different functionalities in single system)



Nanowire FETs

Source: ITRS 2.0 (2015)

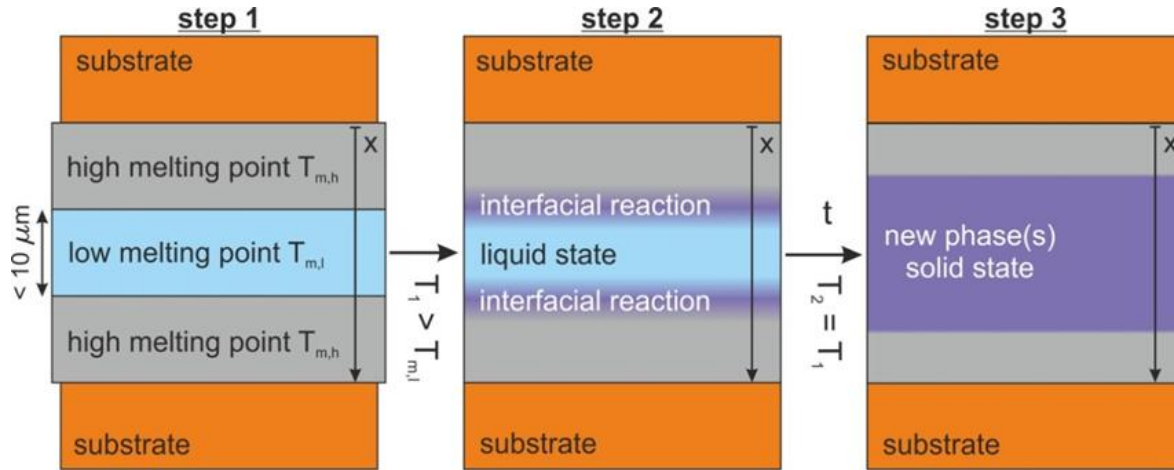


Microfluidic lab-on-a-chip device concept

Source: <http://www.sle.sharp.co.uk>

Transient Liquid Phase (TLP) Bonding

Principal



Basic Principles of the TLP process

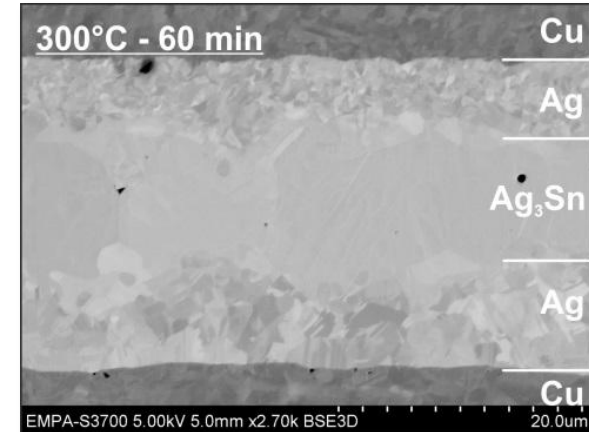
Low-melting metal

- Sn ($T_{m,l} = 232 \text{ } ^\circ\text{C}$)
- In ($T_{m,l} = 157 \text{ } ^\circ\text{C}$)

+

High-melting metal

- Cu, Ag, Au
- Ni ($T_{m,h} = 1455 \text{ } ^\circ\text{C}$)



TLP (Sn; Ag, Ni): $235 \text{ } ^\circ\text{C} \leq T_{\text{process}} \leq 300 \text{ } ^\circ\text{C}$

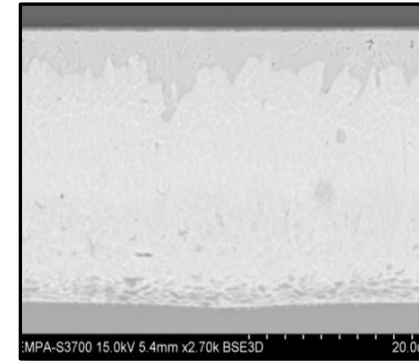
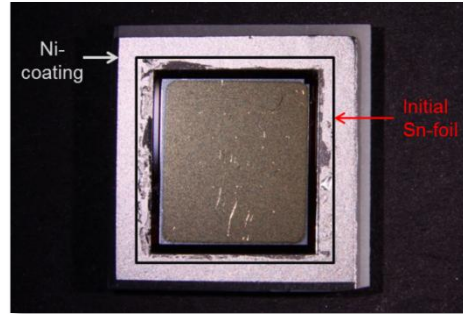
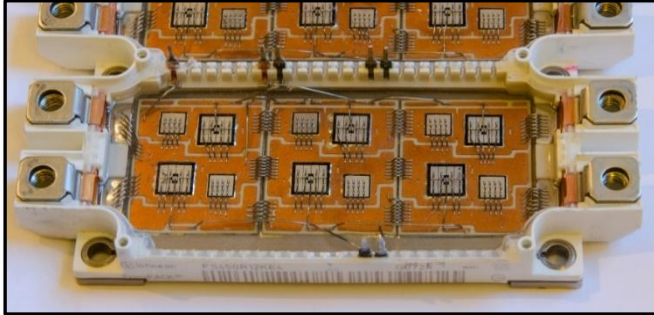
▪ Ag-Sn: formation of $\text{Ag}_3\text{Sn}(\epsilon)$: $T_m = 480 \text{ } ^\circ\text{C}$

▪ Ni-Sn: formation of Ni_3Sn_4 : $T_m = 794.5 \text{ } ^\circ\text{C}$

Transient Liquid Phase (TLP) Bonding

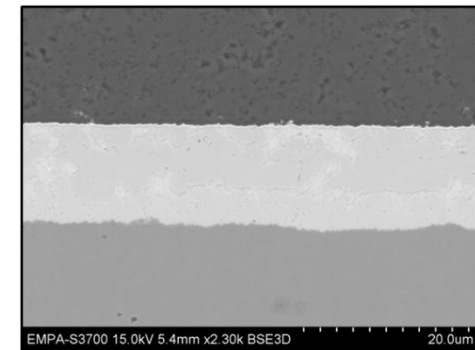
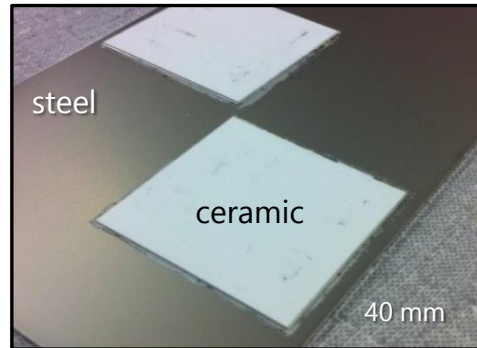
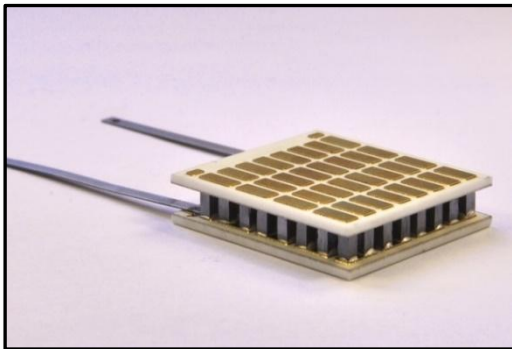
Applications

Ag-Ni-Sn TLP bonding for power electronics



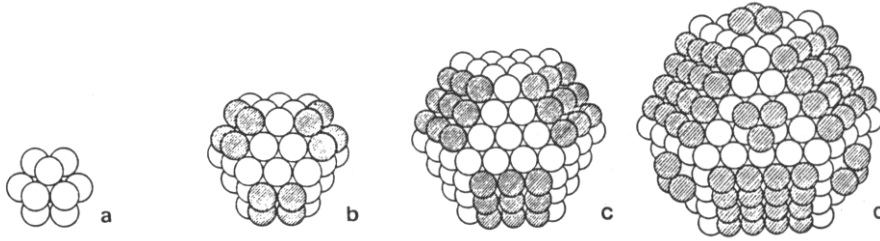
- Si chip
- Ni_3Sn_4
- Ag_3Sn
- Ag

Ni-Sn TLP bonding for thermoelectric module for exhaust applications



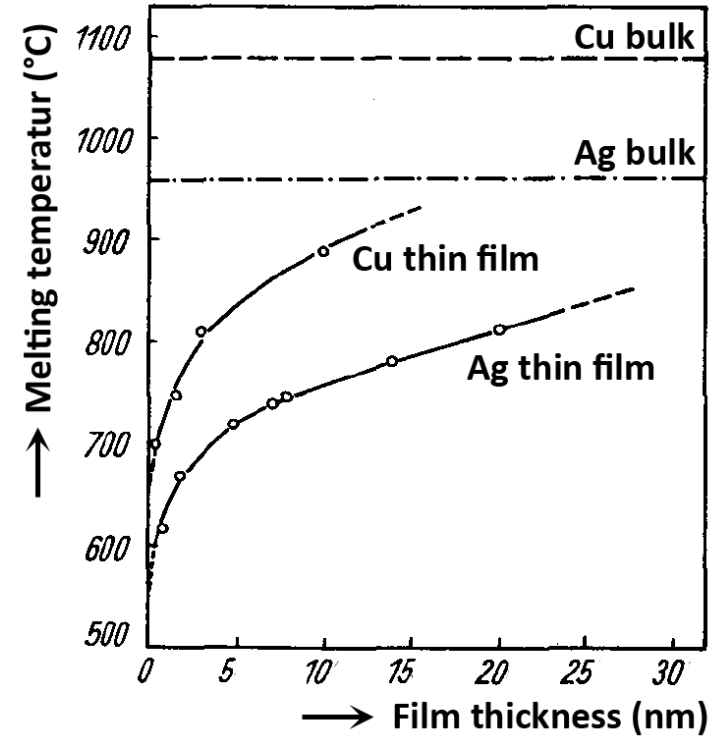
- Al_2O_3
- Ni_3Sn_4
- Ni

Melting Point Depression



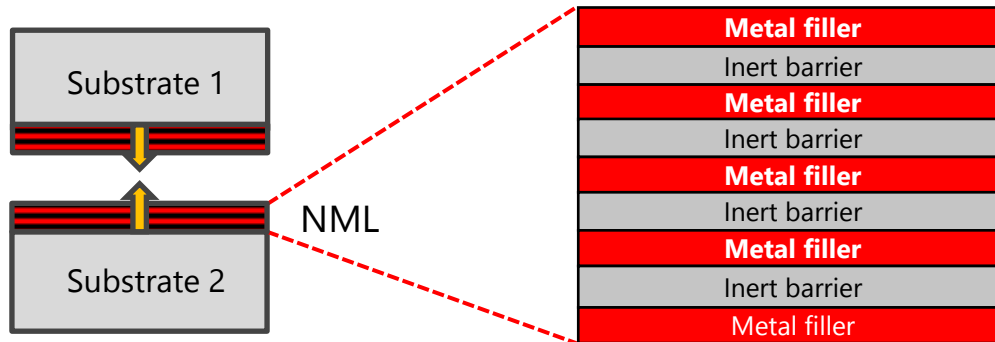
$$\Delta T = (T_S - T) = \frac{2\sigma \cdot T_S}{\rho \cdot L \cdot r} \propto \frac{1}{r}$$

T_S : bulk melting temperature
 σ : solid-liquid interface energy
 L : bulk heat of fusion
 ρ : density of particles
 r : particle radius

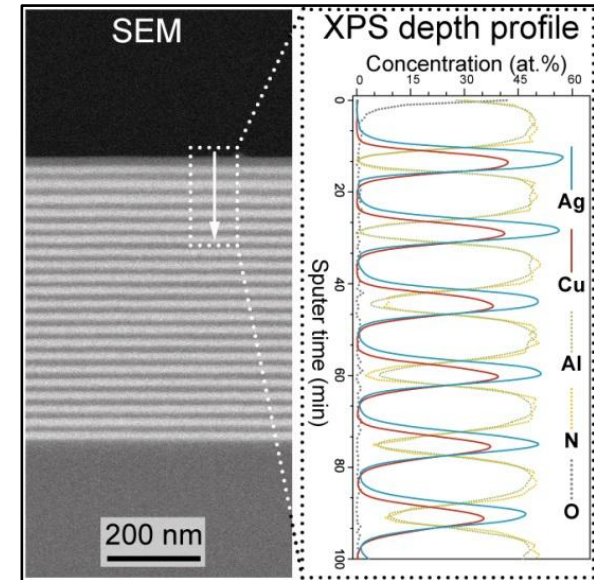


Microstructural design of **Nanomultilayered Fillers** to direct mass transport for localized bonding by exploiting the following nano-scale effects:

- ✓ Fast short circuit diffusion of atoms along internal interfaces
- ✓ Melting point depression of metals and alloys when confined to the nanoscale



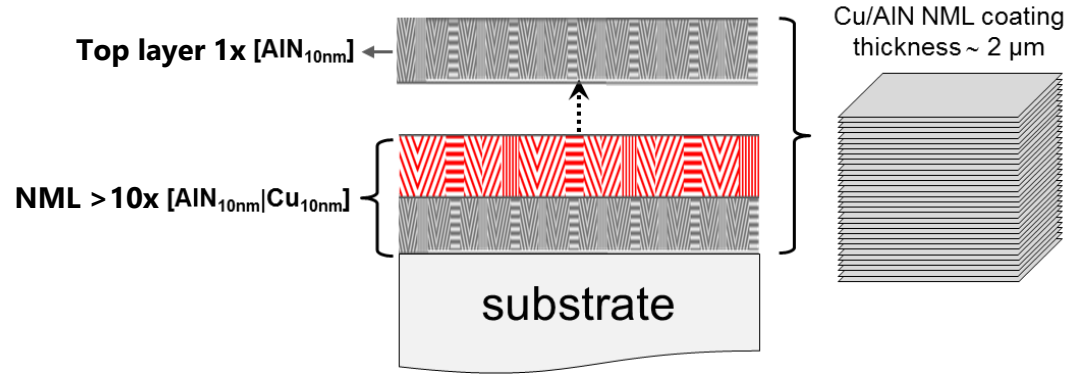
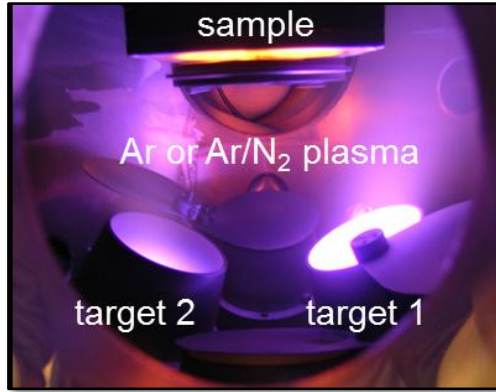
- *J Mater Chem C* 4 (2016), 4927
- *Phys Chem Chem Phys* 17 (2015) 28228
- *Acta Materialia* 107 (2016) 345
- *Scr Mater* 130 (2017) 210
- *J. Mater. Sci. Eng. B* 6 (2016) 226
- *J Mater Eng Perform* 25 (2016) 3275



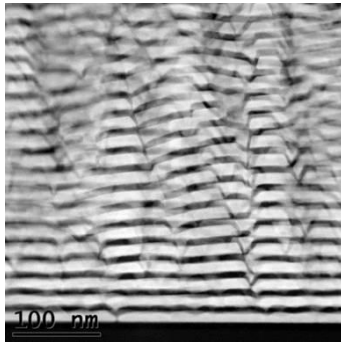
CuAg/AlN NML filler

Nano-joining Approach @ Empa

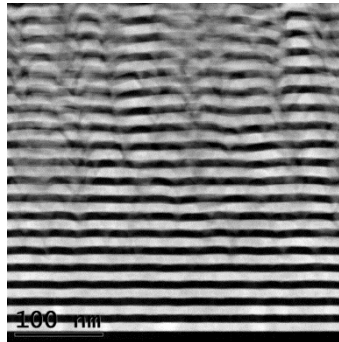
NML Fabrication by DC Magnetron Sputtering



Ag_{10nm}/AlN_{10nm} (dark)



Cu_{10nm}/AlN_{10nm} (20x)



Ag-Cu_{10nm}/AlN_{10nm}



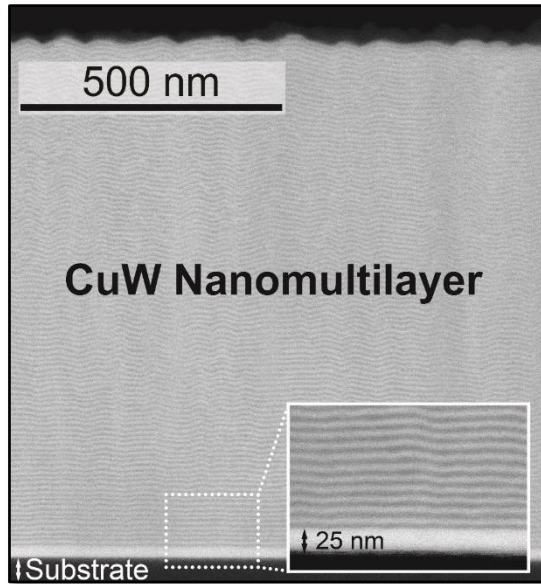
pronounced island growth

interface roughness

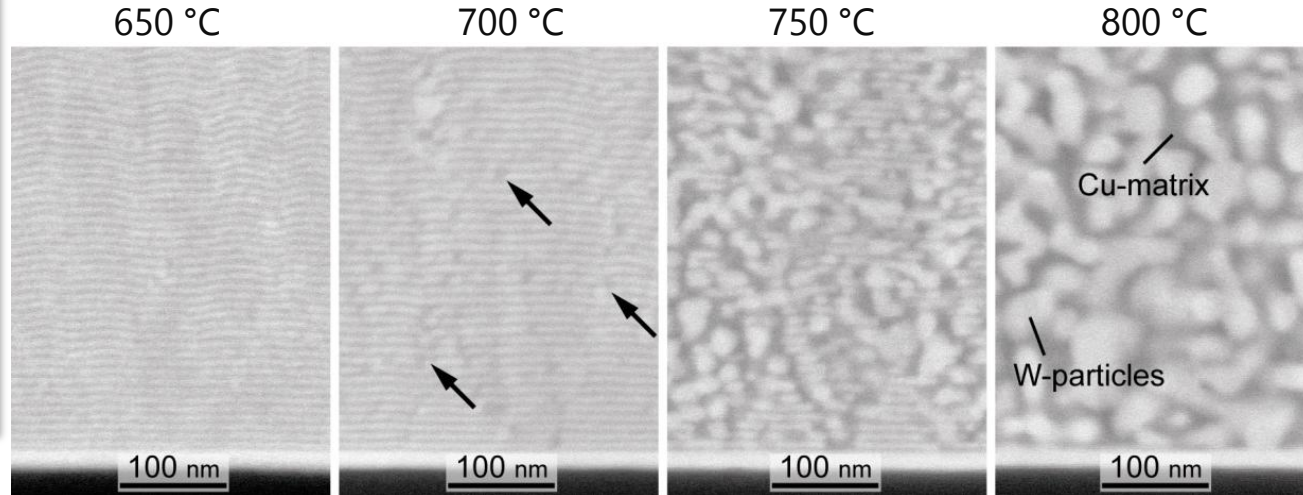
highly uniform layers

Nano-joining Approach @ Empa

Cu/W Nano Multilayer System



$$T_{m,W} = 3422^{\circ}\text{C}$$

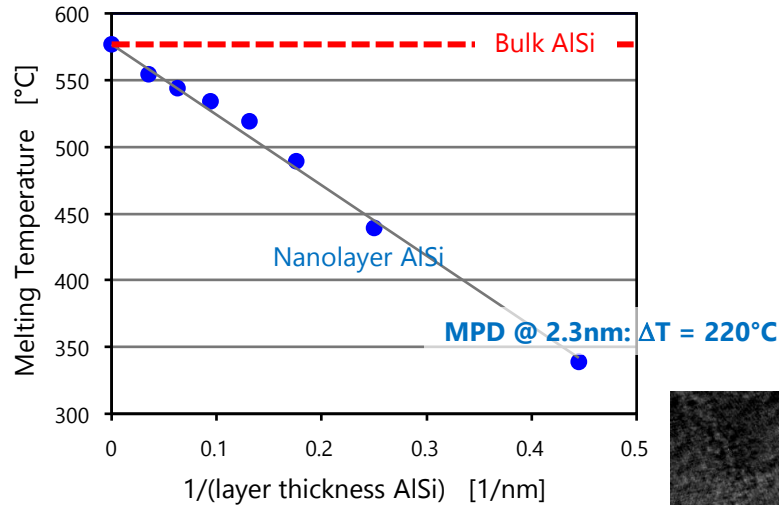


Ref. Acta Materialia 107 (2016) 345

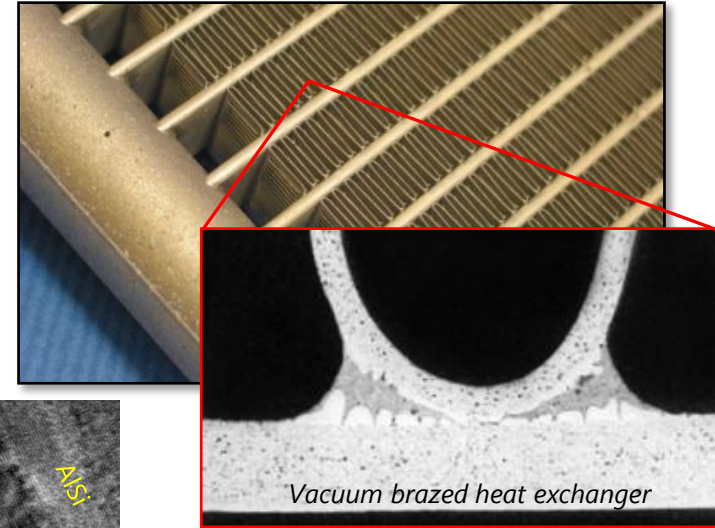
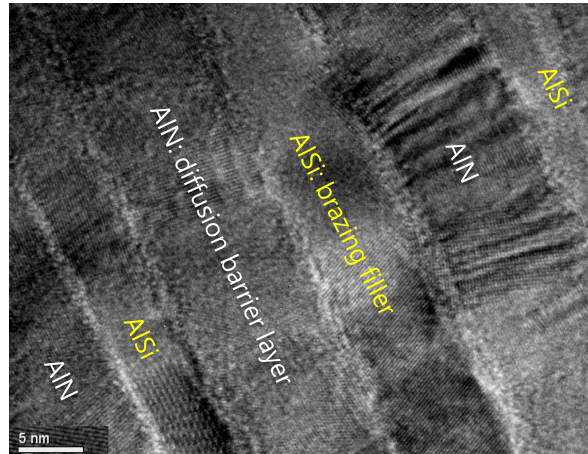
Annealing at $T > 700^{\circ}\text{C}$ leads to gradual degradation of NML into a functional nanocomposite, consisting of globular W particles embedded in Cu matrix.

Nano-Joining

Low-temperature Brazing of Al Alloys (Patent DE102008050433.5)



Ultra-thin Al-Si_{10at.%} films sandwiched between inert AlN diffusion barriers exhibit size-dependent melting point depression (MPD)



References:

- *J Mater Chem C* **4** (2016), 4927
- *Phys Chem Chem Phys* **17** (2015) 28228
- *Acta Materialia* **107** (2016) 345
- *Scr Mater* **130** (2017) 210
- *J. Mater. Sci. Eng. B* **6** (2016) 226
- *J Mater Eng Perform* **25** (2016) 3275

Reactive Joining Systems

Under Study @ Empa

Binary alloy systems

Constituents	Density (g/cm ³)	Heat of reaction (kJ/mole atom)
Al + Pt*	11.63	-100.39
Al + Pd*	7.07	-91.30
3Si + 5Ti	3.72	-72.47
3Si + 5Zr	5.14	-72.10
5Nb + 3Si	6.23	-63.75
Al+Ni*	5.17	-59.17
Al + Co*	5.17	-55.20
2Al + Zr	4.24	-54.09
Al + 2B	2.61	-50.31
2Al + Ti	3.33	-44.61
Al + 3Ni	6.82	-38.25
Al + Ti*	3.63	-37.60
2Al + Zr	4.24	-33.73



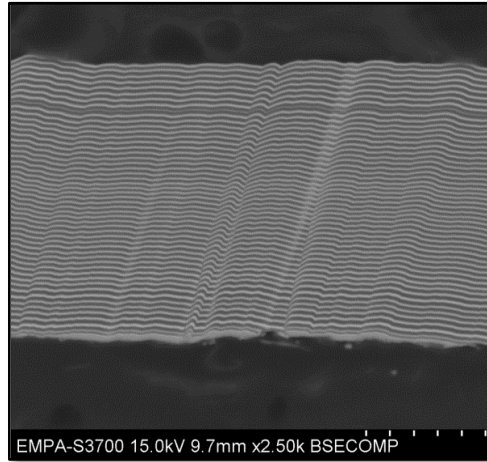
Metal-oxide thermite systems

Constituents	Density (g/cm ³)	Heat of reaction (kJ/mole atom)
2Al + 3CuO	5.11	-149.14
Ti + 2CuO	5.83	-126.57
2Al + Fe ₂ O ₃	4.18	-120.79
3Ti + 2Fe ₂ O ₃	5.01	-91.24
Ti + Fe ₃ O ₄	4.97	-82.31
2Al + Cr ₂ O ₃	4.19	-76.60

Ni-Al Nanofoils© is the only commercially product up to date!

Reactive Joining using Ni-Al Nanofoils[©]

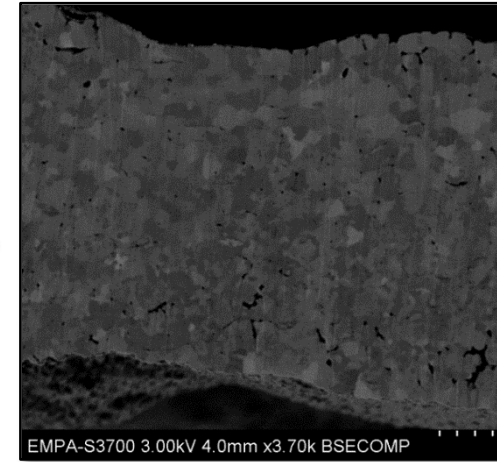
As-deposited Nanofoil[©]



Electric spark ignition



Reacted Nanofoil[©]

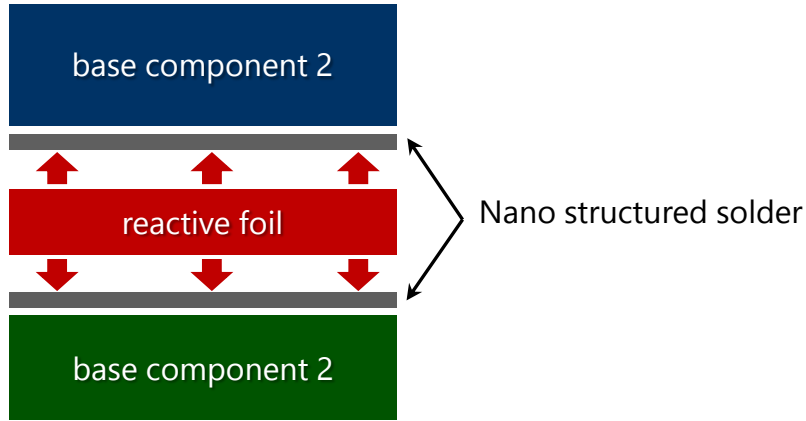


total time: 2.5 milliseconds

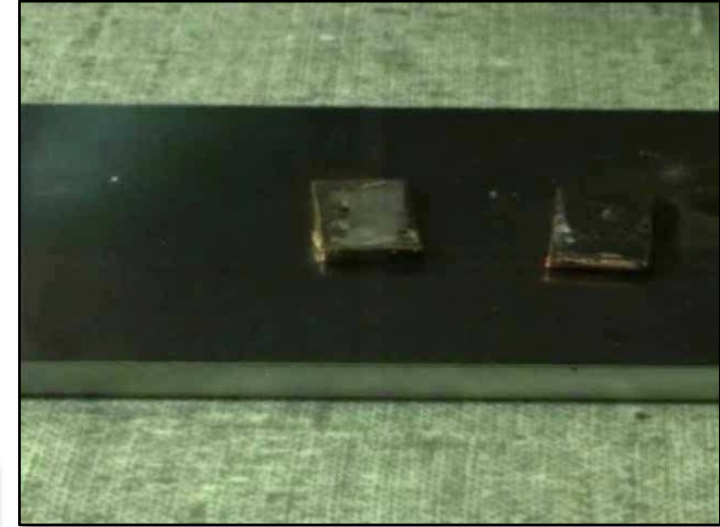
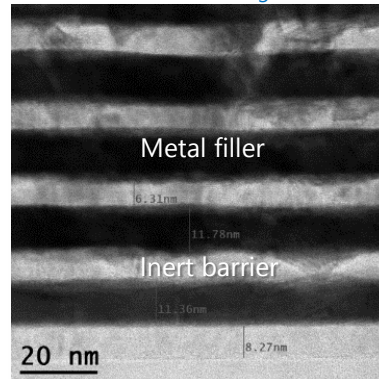
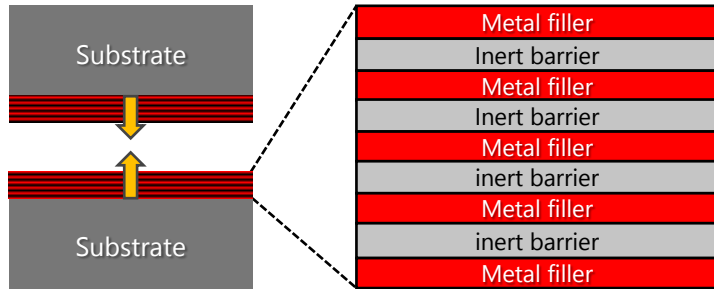
Process characteristics

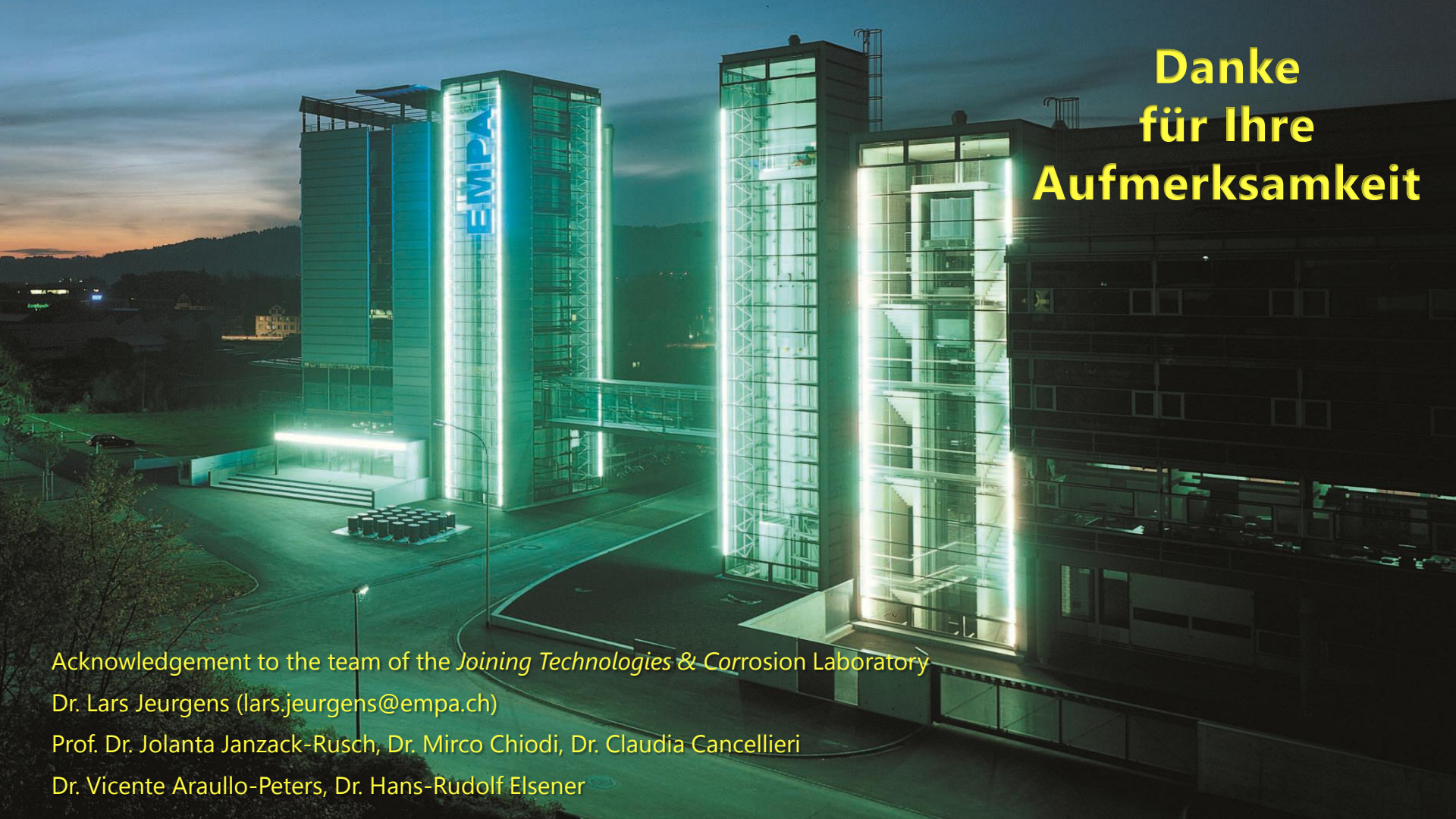
- Local ignition at room temperature with electrical spark, laser pulse or hot filament.
- Self-propagating reaction: **Ni + Al → NiAl** (no gaseous product; heat of reaction ≈ -52 kJ/mol)
- Self-propagating reaction front with temperature > 1000 °C and speed up to 50 m/s!
- Defined heat release by tailoring the overall composition and bilayer thickness

Reactive Nano-Joining



Nano-multilayered fillers ($\text{Ni} + \text{Al} \rightarrow \text{Ni}_3\text{Al}$)





**Danke
für Ihre
Aufmerksamkeit**

Acknowledgement to the team of the *Joining Technologies & Corrosion Laboratory*

Dr. Lars Jeurgens (lars.jeurgens@empa.ch)

Prof. Dr. Jolanta Janzack-Rusch, Dr. Mirco Chiodi, Dr. Claudia Cancellieri

Dr. Vicente Araullo-Peters, Dr. Hans-Rudolf Elsener