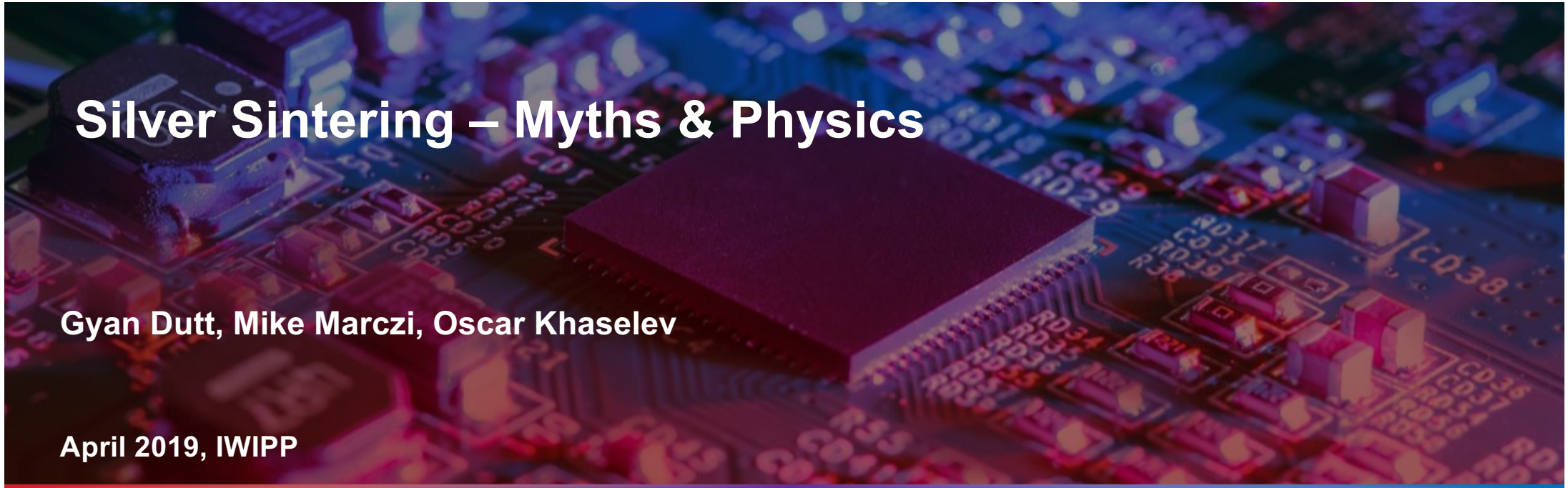

Silver Sintering – Myths & Physics

Gyan Dutt, Mike Marczi, Oscar Khaselev

April 2019, IWIPP

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Silver Sintering - Outline

- Solid State Sintering - Basics
- Myth 1 – Pressure is irrelevant / optional in Sintering
- Myth 2 – Micron & Nano-scale systems are created equal
- Myth 3 – Hybrid sintering is another form of pressure-less sintering
- Summary

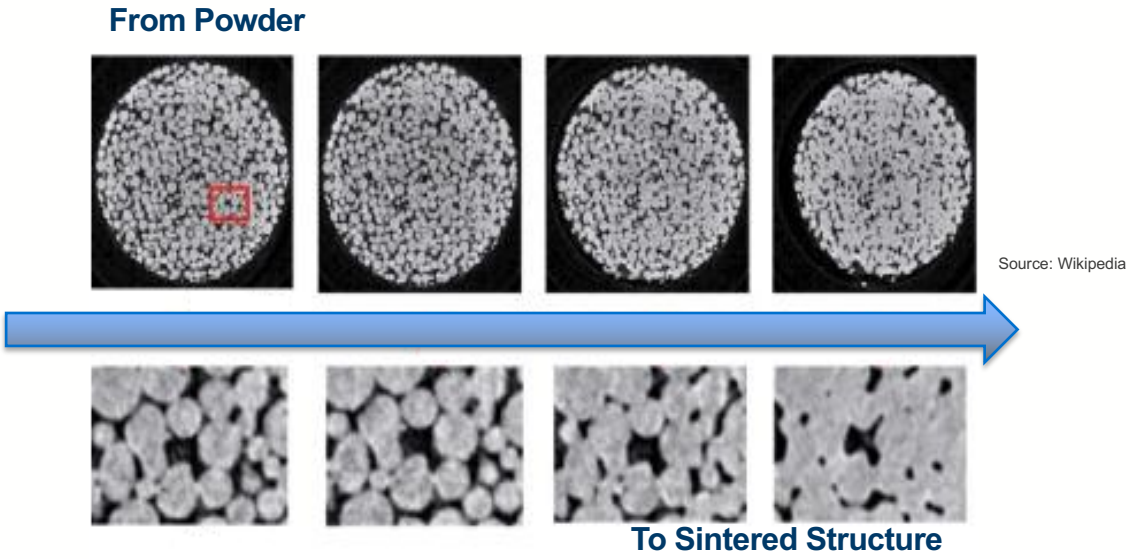
Sintering Basics

(Solid State Sintering Only)

Sintering – Definition

Sintering - method to create structures from powders below melting point

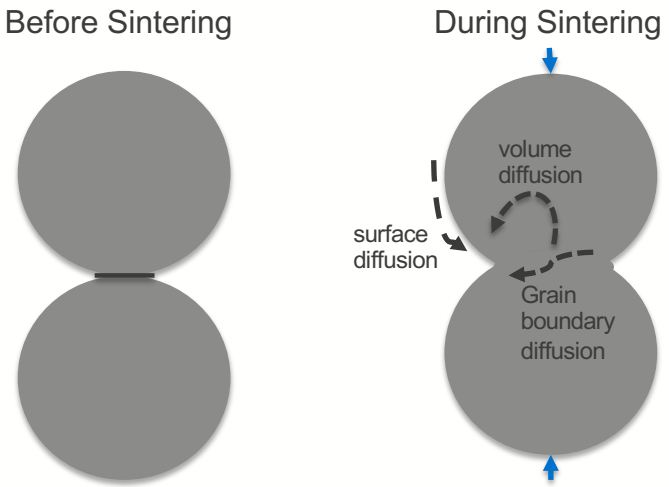
- ❑ Driven by change in Internal Interface / Free Energy
- ❑ Solid State



Sintering – Mechanism

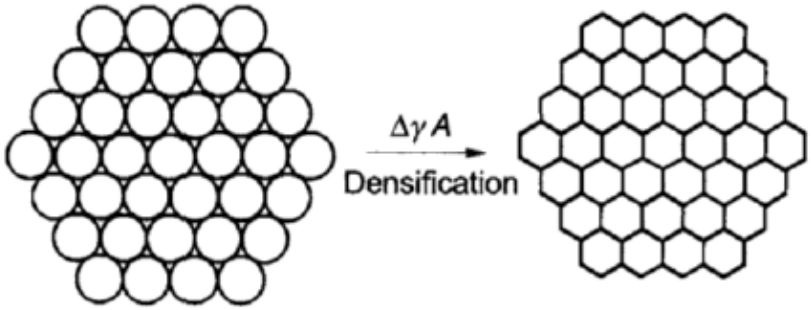
- Underlying mechanism - Mass transport to reduce free surface energy

- Mass transport is facilitated by
  - Diffusion
    - Concentration gradient
    - Pressure Differences
  - Plasticity
    - Dis-agglomeration / Realignment
    - Creep induced by external pressure

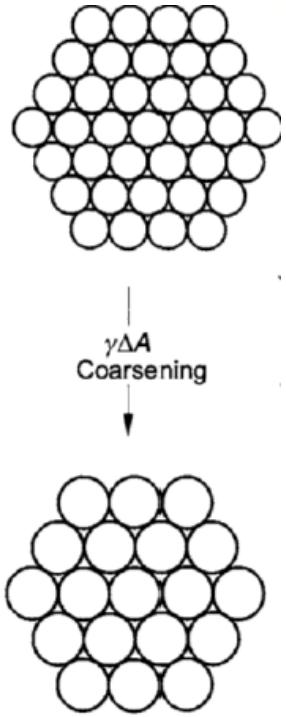


Sintering - Mechanism

- Mass transport results in Grain Growth and Densification



Closing of Pores without Grain Size Increase



Increase in Grain Size without Closing of Pores

Sintering Theory, Peter Derlet, Paul Scherrer Insitut

Sintering Myths 1-3

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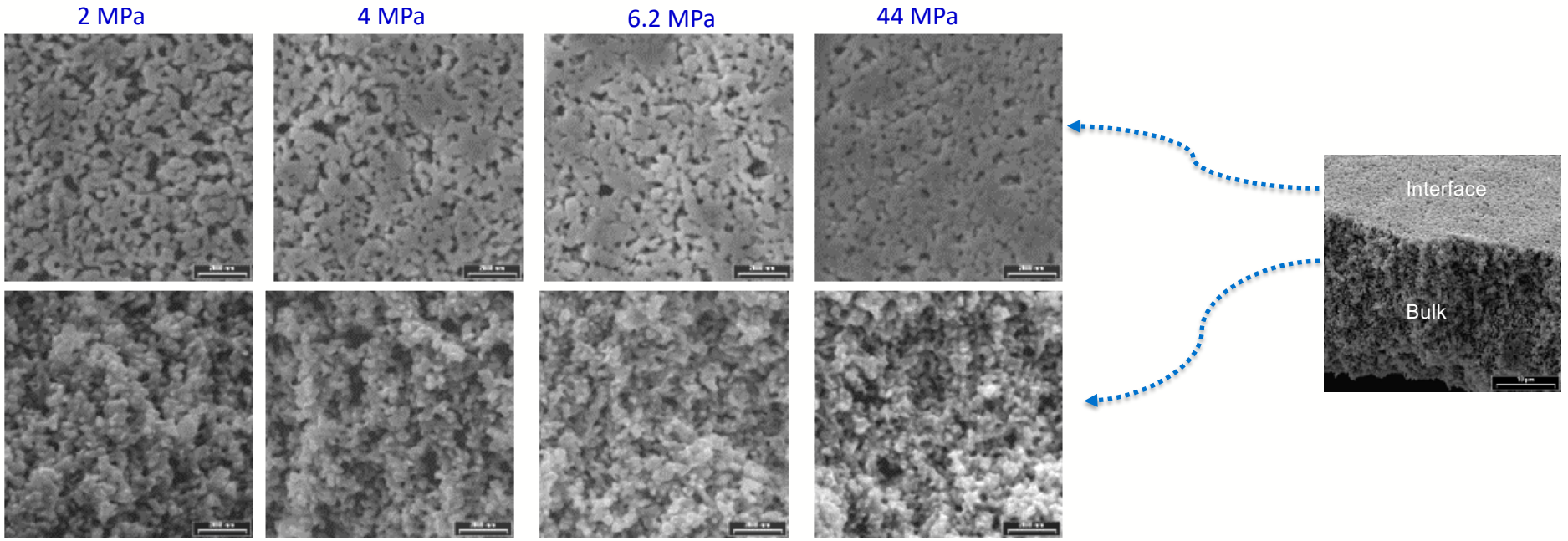
Sintering Myth 1– Pressure is Irrelevant / Optional

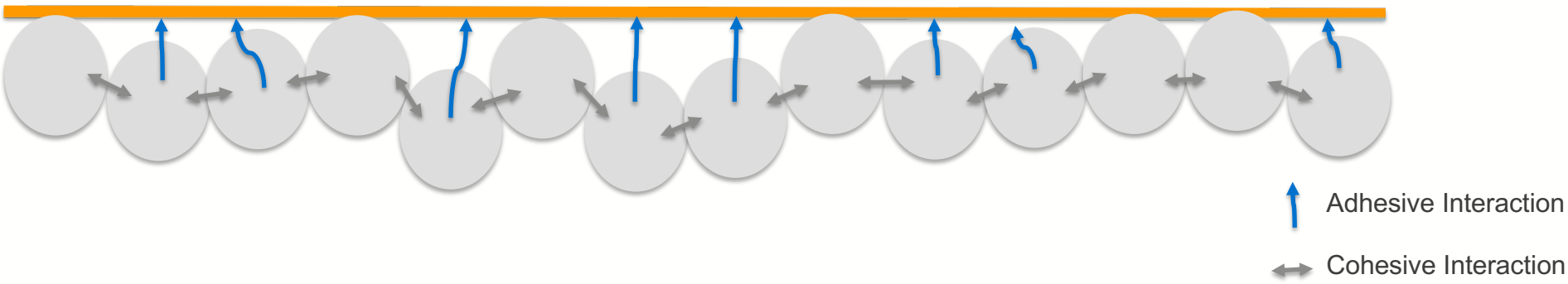


- Sintering pressure promotes diffusion at interface
- Bulk essentially unchanged

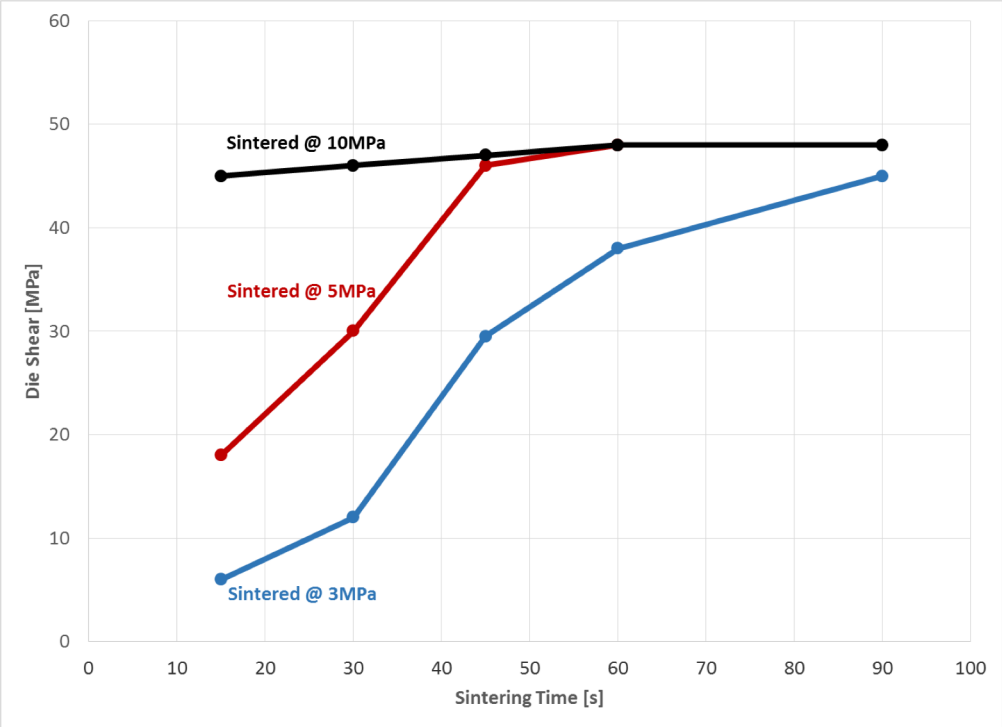
Sintering Myth 1 – Pressure is Irrelevant / Optional

Sintering at Interface vs Bulk – Adhesion vs Cohesion

- Sintering rate at interface is slower (vs bulk)
- Pressure promotes diffusion to the interface – increases probability as well as rate of sintering at interface
- Cohesion – between particles is relatively easy and possible with no pressure



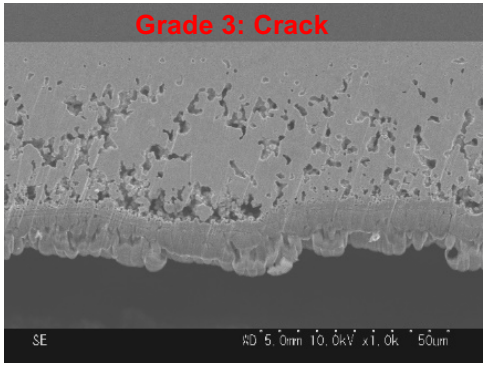
Sintering Myth 1– Pressure is Irrelevant / Optional



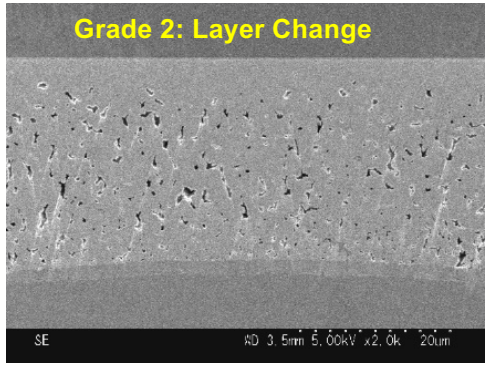
Silver nano-particle system sintered at 250°C

- Pressure enables rapid die shear growth

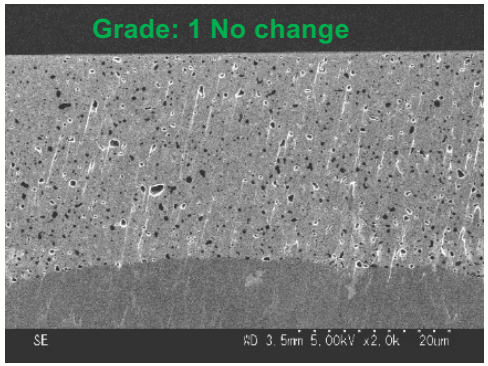
Sintering Myth 1– Pressure is Irrelevant / Optional



2.5 MPa Pressure



5.0 MPa Pressure



10.0 MPa Pressure

AEC-Q100 High Temp Storage Life
Si on Cu substrate

- Pressure enables stable structure – even for bare Cu
- Prevents corrosion from trapped O_2 – key to achieving automotive grade reliability

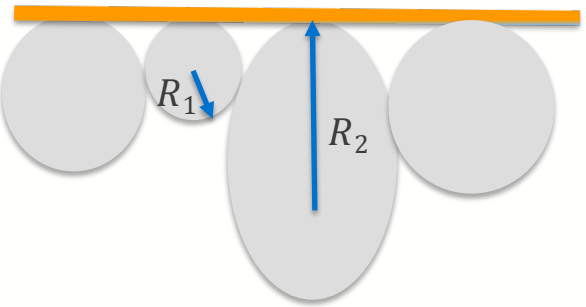
Sintering Myth 2 – Micron & Nano are created Equal

- Thermodynamic driving force extremely large for sintering nano particles

$$\sigma = \gamma\left(\frac{1}{R_1} + \frac{1}{R_2}\right)$$

σ = surface energy reduction
γ = particle surface energy

German, R. M. 1996. *Sintering - Theory and Practice.* Wiley-Interscience.

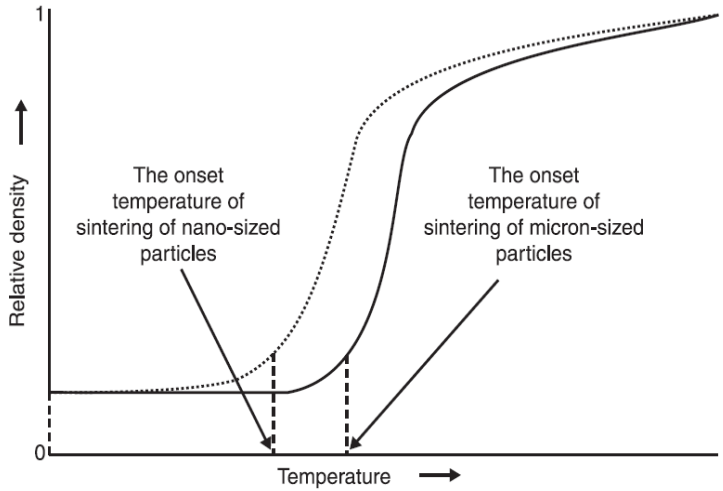


$$\frac{\Delta t_2}{\Delta t_1} = \frac{R_2}{R_1}$$

C. Herring, J. Appl. Physics, 1950.

- Mass Transport increases exponentially (non-linear diffusion) with reduction in particle size
- Surface energy substantially higher for smaller particle sizes
- Nanoparticle diffusion at interface is more rapid than micron

Sintering Myth 2 – Micron & Nano are created Equal

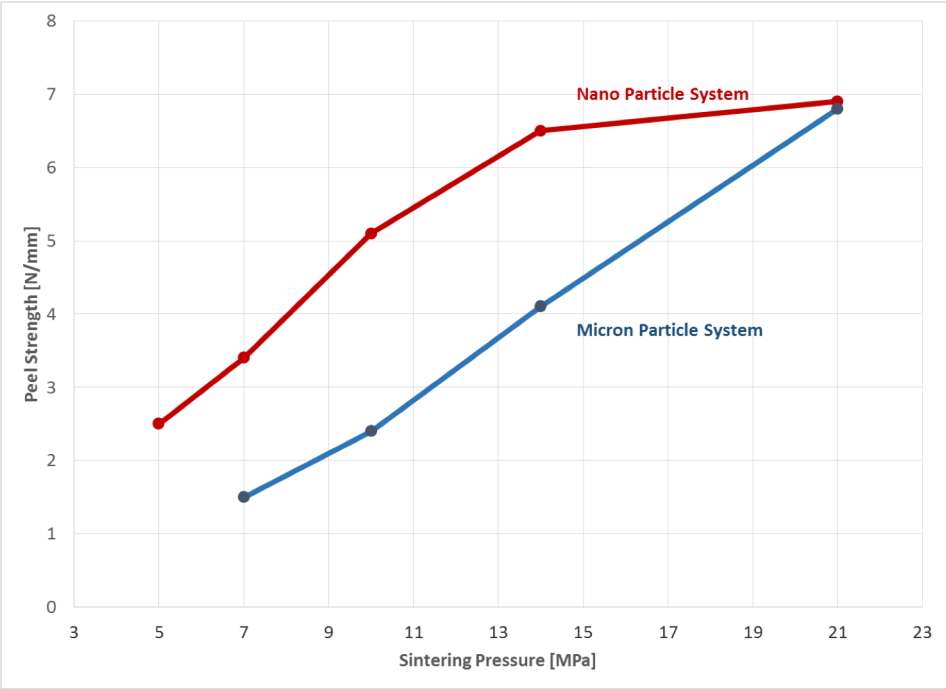


Wang, Z.Z., and H. Fang. 2010. "Sintering of ultrafine and nanosized particles." In *Sintering of advanced materials*, 434-473. Wooodhead Publishing Limited.

Sintering temperature decreases steadily for particles smaller than 1um

- Nanoparticles sinter at lower temperatures (compared to micron scale)

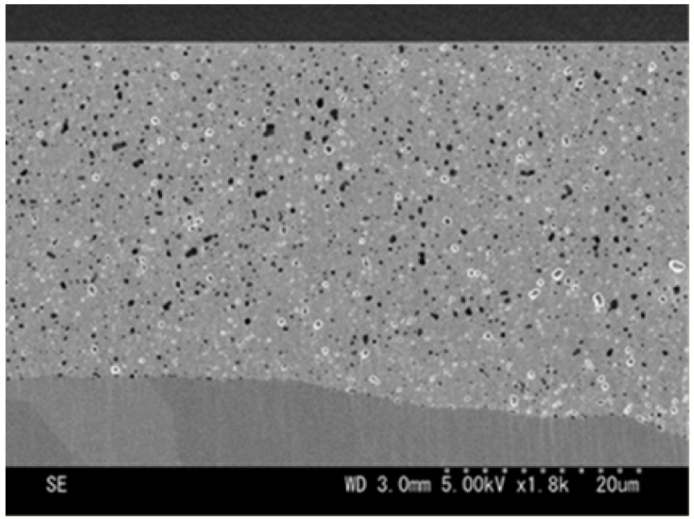
Sintering Myth 2 – Micron & Nano are created Equal



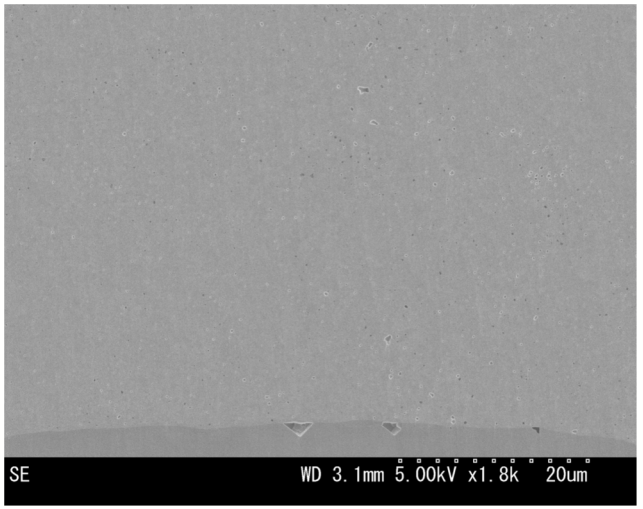
- Nano particle systems sinter at lower pressure

Sintering Myth 2 – Micron & Nano are created Equal

Nano 10MPa



Micron 20MPa

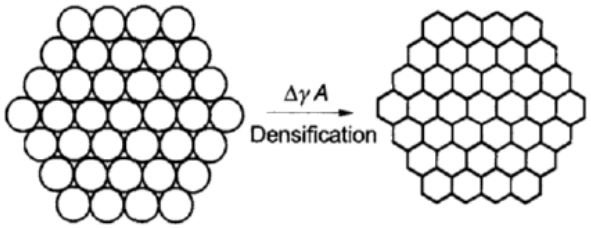


- Nano-particle system has “sponge-like” structure - finely distributed porosity with lower modulus (12-15 Gpa)
- Micron-scale system is highly dense with coarser grains and high modulus (>35 Gpa)

Material System	Modulus (GPa, 25°C)
Lead-free Solder	26-80
Silver Epoxy	4-20
Hybrid Silver Sintering	18
Micron Sintered	>35
Nano Sintered	12-15
Silver	>80

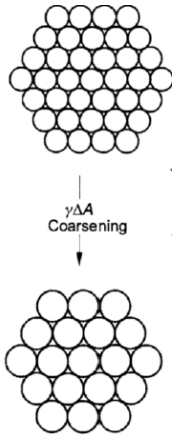
Grain Growth vs Densification

Densification



- Happens throughout sintering cycle – but dominant in later stages
- Pressure assists in densification – by particle rearrangement and creep AND enabling sintering at lower temperatures (slower kinetics)
- Results in lower modulus “sponge” structure

Grain Growth



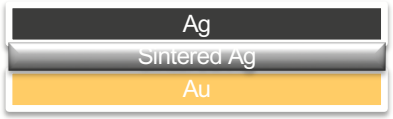
- Dominant in early and intermediate stages of sintering cycle
- Pressure arrests grain growth (lower temperature & shorter time) and reduces grain boundary mobility
- Longer sintering time aids coarsening
- Results in higher modulus structure

Silver Sintering on Different Surfaces

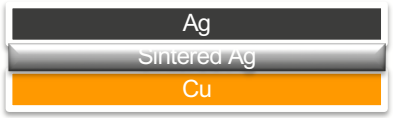
$$D = D_0 e^{E}_{RT}$$

Ag $D = 0.4e(^{-44090}_{RT})$

Au $D = 0.047e(^{-38500}_{RT})$



Cu $D = 0.02e(^{-35600}_{RT})$



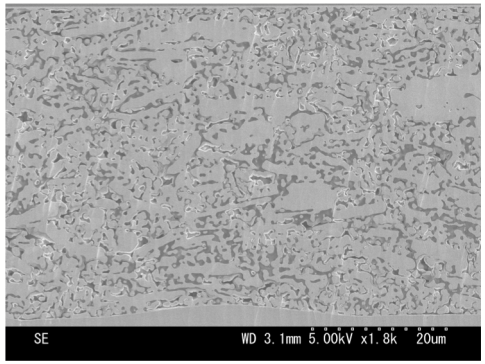
Diffusion Coeff Ag ~8X Au

Diffusion Coeff Ag ~ 20X Cu

- Diffusion rates are different for different metallized surfaces
- For Cu - much harder to control grain size and porosity without pressure and micron size

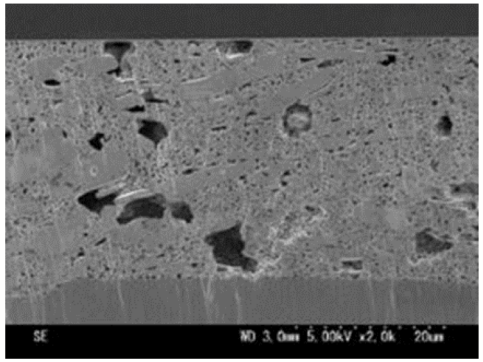
Sintering Myth 3 - Hybrid / Semi Sintering is another form of “Pressure-less Sintering”

Hybrid Sintered



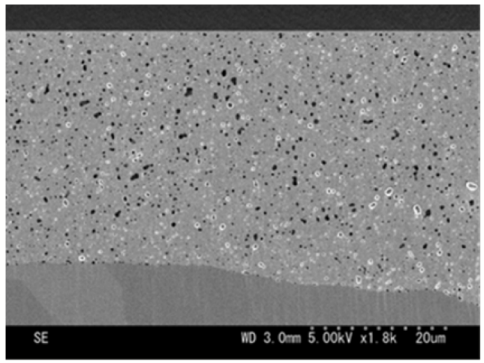
- Limited solid state diffusion between particles
- Higher thermal resistance at particle-to-particle interfaces and metallization
- Coarse uneven grains

High Silver Conductive Epoxy



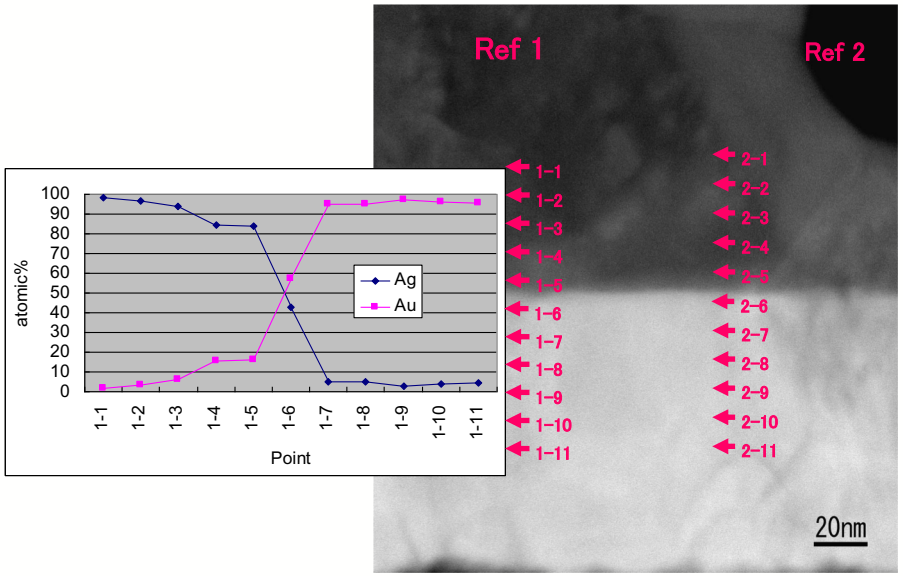
- Solid state diffusion with uneven porosity
- Inconsistent bonding at metallization
- Weaker interface with higher resistance

Pressure Sintered

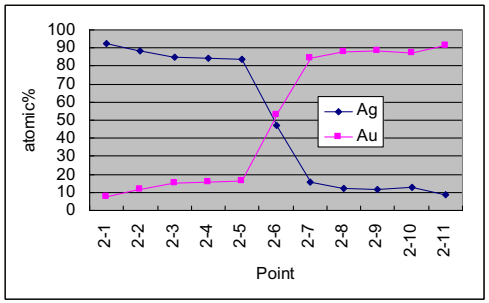


- 100% solid state diffusion
- Small pores with small grain size
- Ohmic contact at interface Low thermal resistance
- Low modulus & low stress

Sintering Myth 3 – Closer look at Interface….



point	Ag-L	Au-L
ref1	98.8	1.2
ref2	93.8	6.2



- Sintering without resin enables pure metallic diffusion bond without any intermetallics
- Rapid transition between metallization and sintered layer (<40nm)

Summary / Take-Aways

- ❑ Pressure is key to controlling diffusion at interface and grain-growth
  - ❑ Aids in closing the porosity at interfaces (both adhesion & cohesion)
  - ❑ Controlling the grain size – especially for nano-systems

- ❑ Starting particle size is key to controlling the structure
  - ❑ Nano-pressure system has lower modulus "sponge"- like structure
  - ❑ Micron structure is highly dense but very coarse

- ❑ Hybrid / Semi sintering systems are poor substitute to resin-free systems
  - ❑ Limited sintering with weak interface
  - ❑ Non-metallic high thermal resistance

Thank you

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