# DOE MURI:
# Hig-Operating Temperature Heat Transfer Fluids for CSD Applications

**Project start date: October 1, 2012**

**DOE SunShot Concentrating Solar Power Program Review**

**April 23rd - 25th, 2013**
**Phoenix, AZ**

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# Liquid Metals as Advanced High-Temperature Heat Transfer Fluids

- **Good (potential) thermal stability:**

  **High boiling points**
  **Low vapor pressures**

- **Excellent transport properties:**

  **High thermal conductivity (compact heat exchangers)**

  **Low viscosity**

- **Vast compositional spaces:**

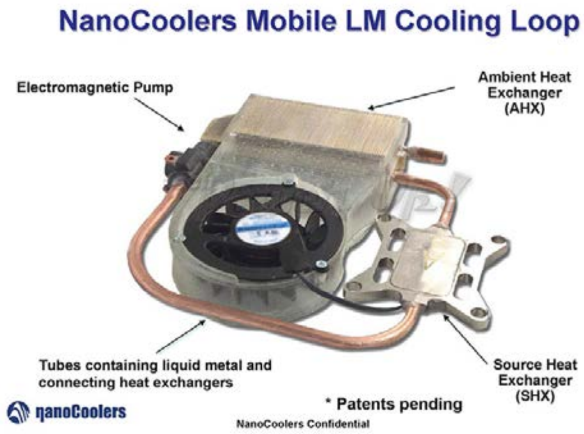
  **Tailored alloy compositions for**

    **low melting points**
    **improved material compatibility**

# Past and On-going Studies on Liquid Metals

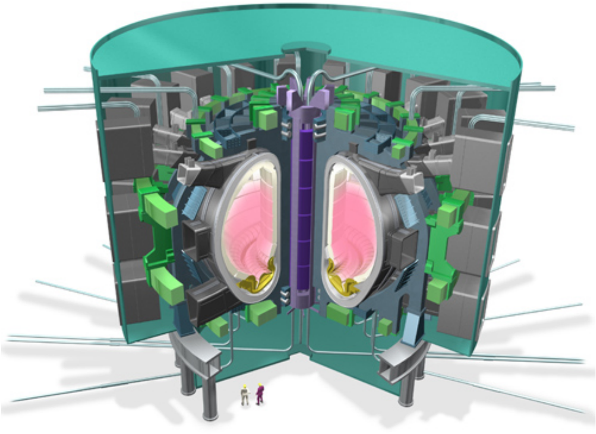
## Space/submarine nuclear power

## Electronics thermal management




## Next generation nuclear fission reactor

## Nuclear fusion reactor



# Technical Targets of the Proposed Work

| | Technical Targets |
|---|---|
| Thermal Stability (as a liquid) | ≥ 800°C<br>(Stretch Target: ≥ 1300°C) |
| Melting Point | ≤ 100°C |
| Vapor Pressure | ≤ 0.01 atm |
| Viscosity | ≤ 2 mPa s at 300 °C and 600 °C |
| Volumetric Heat Capacity | > 2 $MJ/m^3$ K |
| Thermal Conductivity | > 10 W/m K |
| Materials Compatibility | Carbon Steel (< 425°C), Stainless Steel (< 650°C), and High-temperature Alloys |
| Safety | No or manageable environmental/health hazard |
| Cost | ≤ $1/kg |

# Characteristics of an Existing Liquid Metal

| | Technical Targets | Pb-Bi Eutectics (LBE) |
|---|---|---|
| Thermal Stability (as a liquid) | ≥ 800°C<br>(Stretch Target: ≥ 1300°C) | Boiling point = 1670 °C<br>(limited by corrosion to < 600 °C) |
| Melting Point | ≤ 100°C | 125°C |
| Vapor Pressure | ≤ 0.01 atm | ~ 0.01 atm at 1100 °C |
| Viscosity | ≤ 2 mPa s at 300 °C and 600 °C | 1.8 mPa s at 300 °C, 1.2 mPa s at 600 °C |
| Volumetric Heat Capacity | > 2 MJ/$m^3$ K | ~ 1.5 MJ/$m^3$ K |
| Thermal Conductivity | > 10 W/m K | 12 W/m K at 300 °C<br>16 W/m K at 600 °C |
| Materials Compatibility | Carbon Steel (< 425°C), Stainless Steel (< 650°C), and Nickel Alloys | Manageable at temperatures only up to ~ 600 °C |
| Safety | No or manageable environmental/health hazard | toxic only if ingested |
| Cost | ≤ $1/kg | < $10/kg (estimate) |

# Scientific and Engineering Challenges

- Develop low-melting point liquid metals that are either intrinsically corrosion resistant or capable of forming robust passivation layers for reliable operations at temperatures > 800 °C.
- Identify best commercial structural materials to go with the new liquid metals.
- Reduce the cost of liquid metals (and companion structural materials).
- Eliminate/control the environmental/health impact.
- Enhance the heat capacity of liquid metals.

❖ Past and on-going research on liquid metals were limited to temperatures < 600 °C and focused almost exclusively on nuclear applications, restricting permissible elements and compositional spaces.

❖ High-throughput combinatorial synthesis and characterization capability can dramatically accelerate material evaluation and development.

# Higher Demand Satisfied with More and More Complex Materials

- **Steels:** $Fe_{98}C_2$ => $Fe_{66}W_{17}Cr_{10}C_{3.5}Mo_{2.5}$, Christite 1
- **Superconductor:** Nb => $HgBa_2Ca_2Cu_3O_x$, High-Tc Superconductor
- **Metallic Glasses:** $Au_{80}Si_{20}$ => $Au_{49}Ag_{5.5}Pd_{2.3}Cu_{26.9}Si_{16.3}$
- **Dental:** Au => $Au_{75}Pd_{18.5}Ag_{1.5}Ir_{0.01}Ru_{0.05}In_2Sn_2Cu_{0.44}Zn_{0.5}$

# Daunting Task

**If we assume we create new alloys with every 1 atomic % change in composition, we need to examine**

- **for three elements,  ~ 5000 ternary alloys**
- **for four elements,  ~ 150,000 quaternary alloys**
- **for five elements,  ~ 3,500,000 quinary alloys**
- **for six elements, ~ 70,000,000 senary alloys**

**If we have 10 elements,**

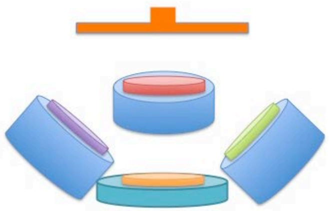
**150,000 * (10*9*8*7)/(4*3*2*1) = 31,500,000 quaternary alloys**

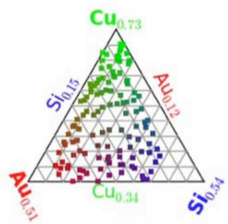
**Only infinitesimal fraction of composition space have been considered!**

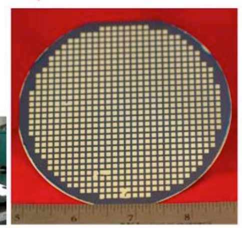
# Approach / Research Tasks

**Thermochemical modeling (UCB)**

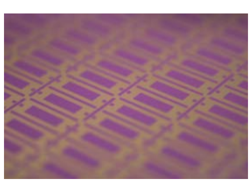
**Combinatorial thin-film synthesis (Yale)**

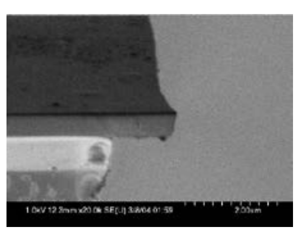




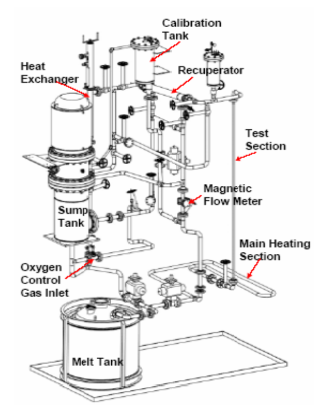
**High-throughput property characterization (UCLA and Yale)**

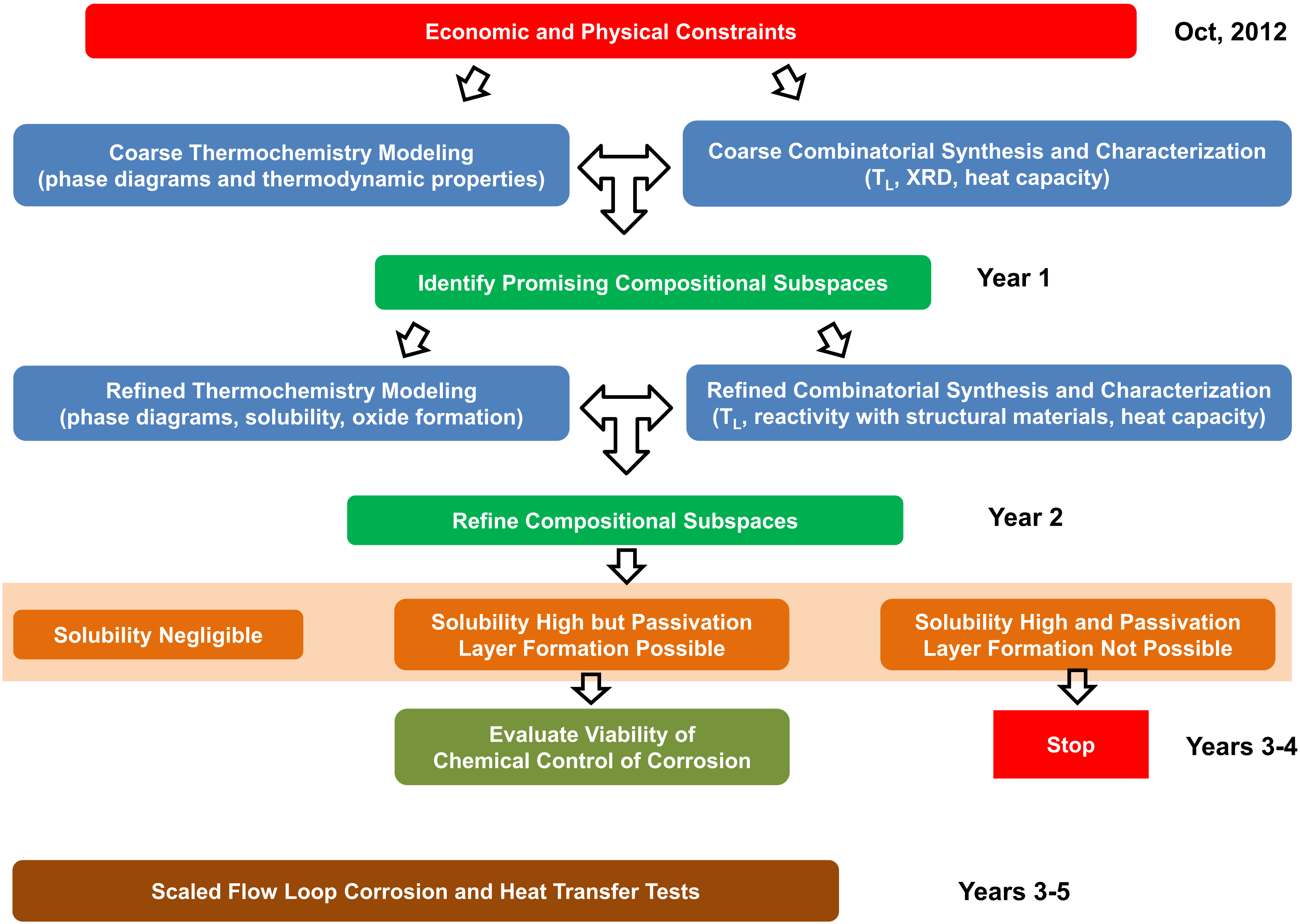




**Static corrosion testing (UCB)**

**Flow loop testing/ Heat transfer characterization (UCLA)**




Economic and Physical Constraints
Oct, 2012
Coarse Thermochemistry Modeling
(phase diagrams and thermodynamic properties)
Coarse Combinatorial Synthesis and Characterization
($T_L$, XRD, heat capacity)
Identify Promising Compositional Subspaces
Year 1
Refined Thermochemistry Modeling
(phase diagrams, solubility, oxide formation)
Refined Combinatorial Synthesis and Characterization
($T_L$, reactivity with structural materials, heat capacity)
Refine Compositional Subspaces
Year 2
Solubility Negligible
Solubility High but Passivation
Layer Formation Possible
Solubility High and Passivation
Layer Formation Not Possible
Evaluate Viability of
Chemical Control of Corrosion
Stop
Years 3-4
Scaled Flow Loop Corrosion and Heat Transfer Tests
Years 3-5

# Thermochemical Considerations

Na Mg K Ca
Cu Zn Cd Al
Sn Sb Pb Bi

1. Based solely on melting temperature, cost and toxicity, 11 elements were identified as favorable candidates.

2. Some elements ruled out due to high solubility of Fe (piping material) in their melt phase

Na Mg K Ca
Cu Zn Cd Al
Sn Sb Pb Bi

Na Mg K Ca
Cu Zn Cd Al
Sn Sb Pb Bi

3. Some of elements ruled out in step 2 added back into consideration because of possibility of forming passivation layers

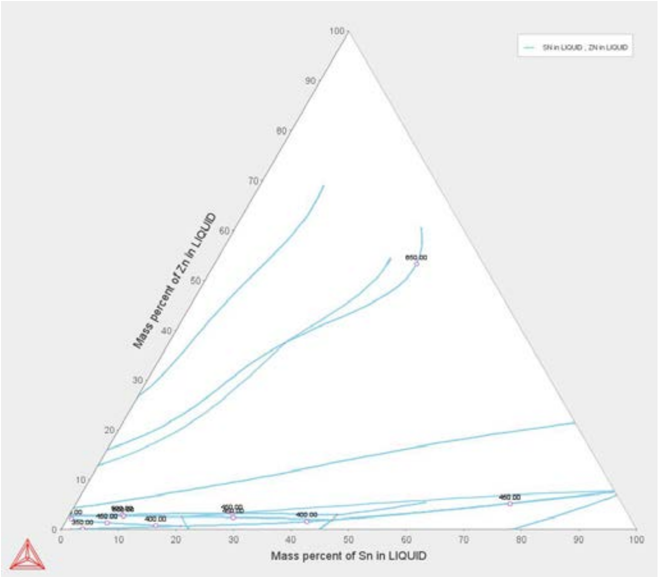
4. Best binaries so far are systems containing Bi and Pb. Cadmium demonstrates the required properties as well.

Bi – Pb
Bi – Cd
Bi – Sn
Ca – Cu

## Thermocalc

- Framework for modeling thermochemistry and phase stability of multicomponent systems
- Use to identify promising compositions with low eutectic temperatures and oxidation characteristics

Calculated Bi-Sn-Zn Liquidus Projection

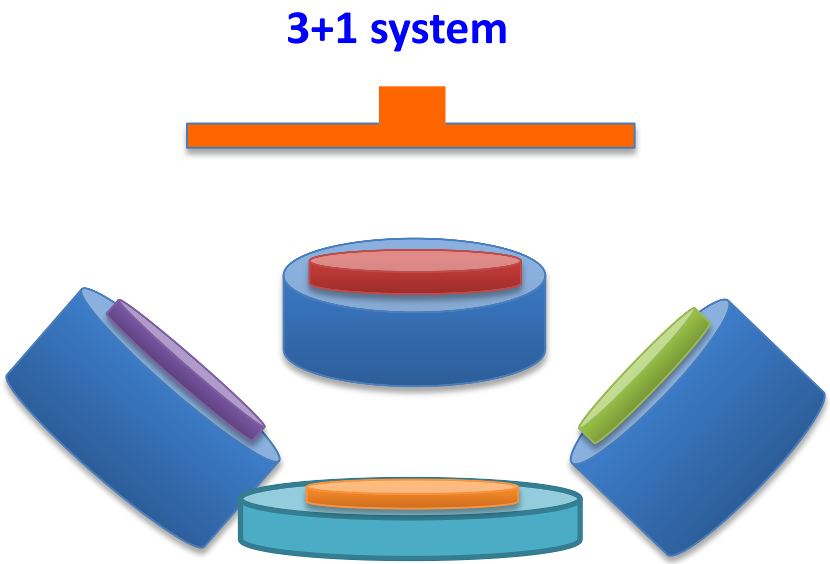


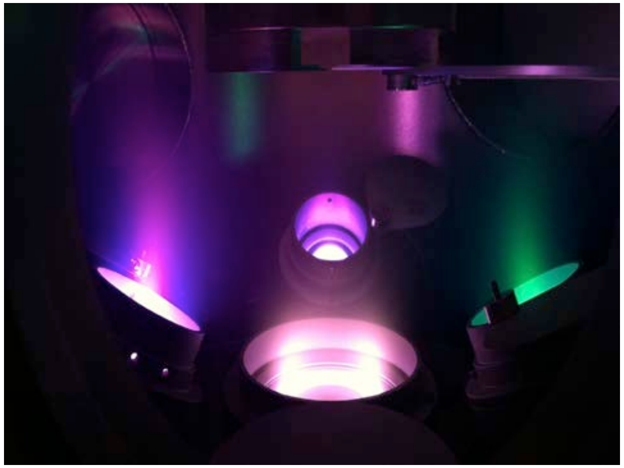
# Combinatorial Synthesis of Candidate Alloys

❖ Co-sputtering of composition libraries.

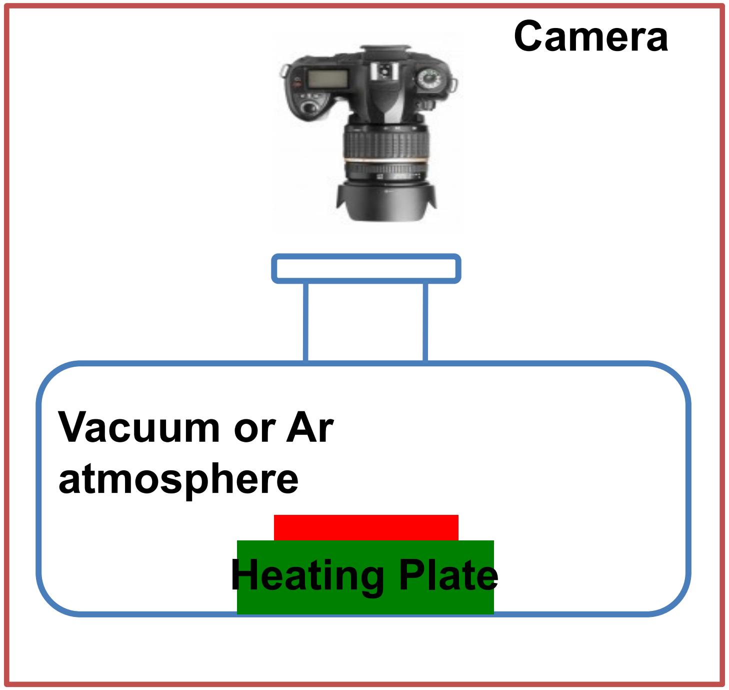
❖ 3 gradient guns with tilt capability for 0~50% compositional variations over 4-inch substrates.

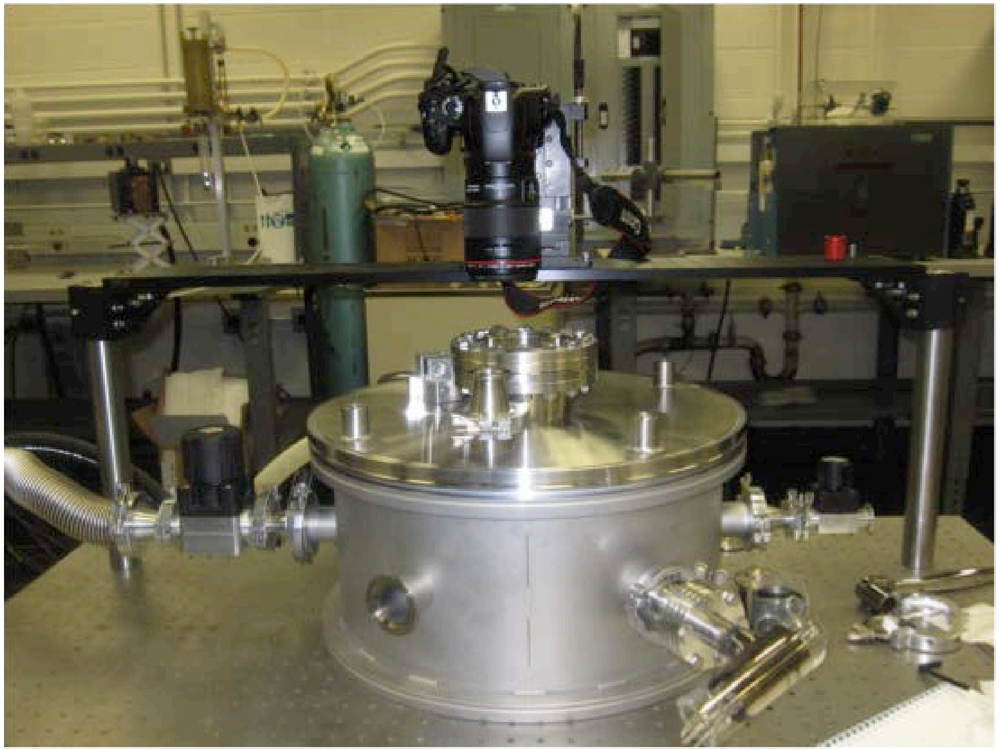
❖The 4th gun allows uniform deposition of another element or base alloys of fixed compositions.



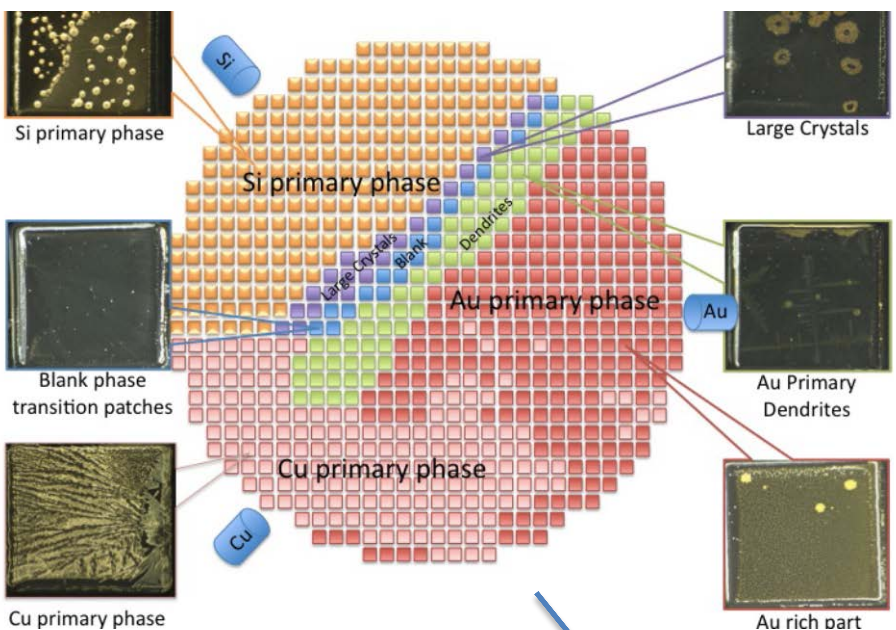
# High Throughput Characterization of Liquidus Temperatures



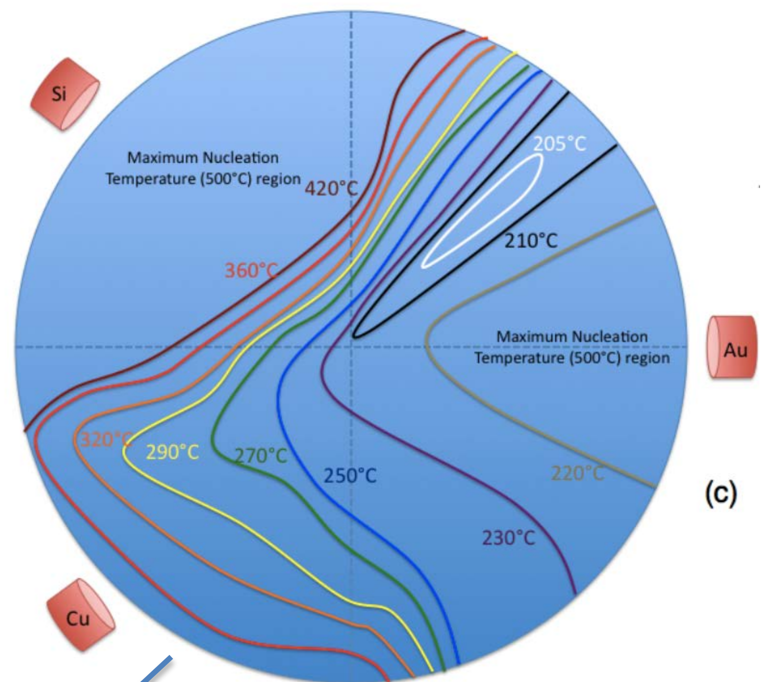



# High Throughput Characterization of Liquidus Temperatures: Bulk Metallic Glasses

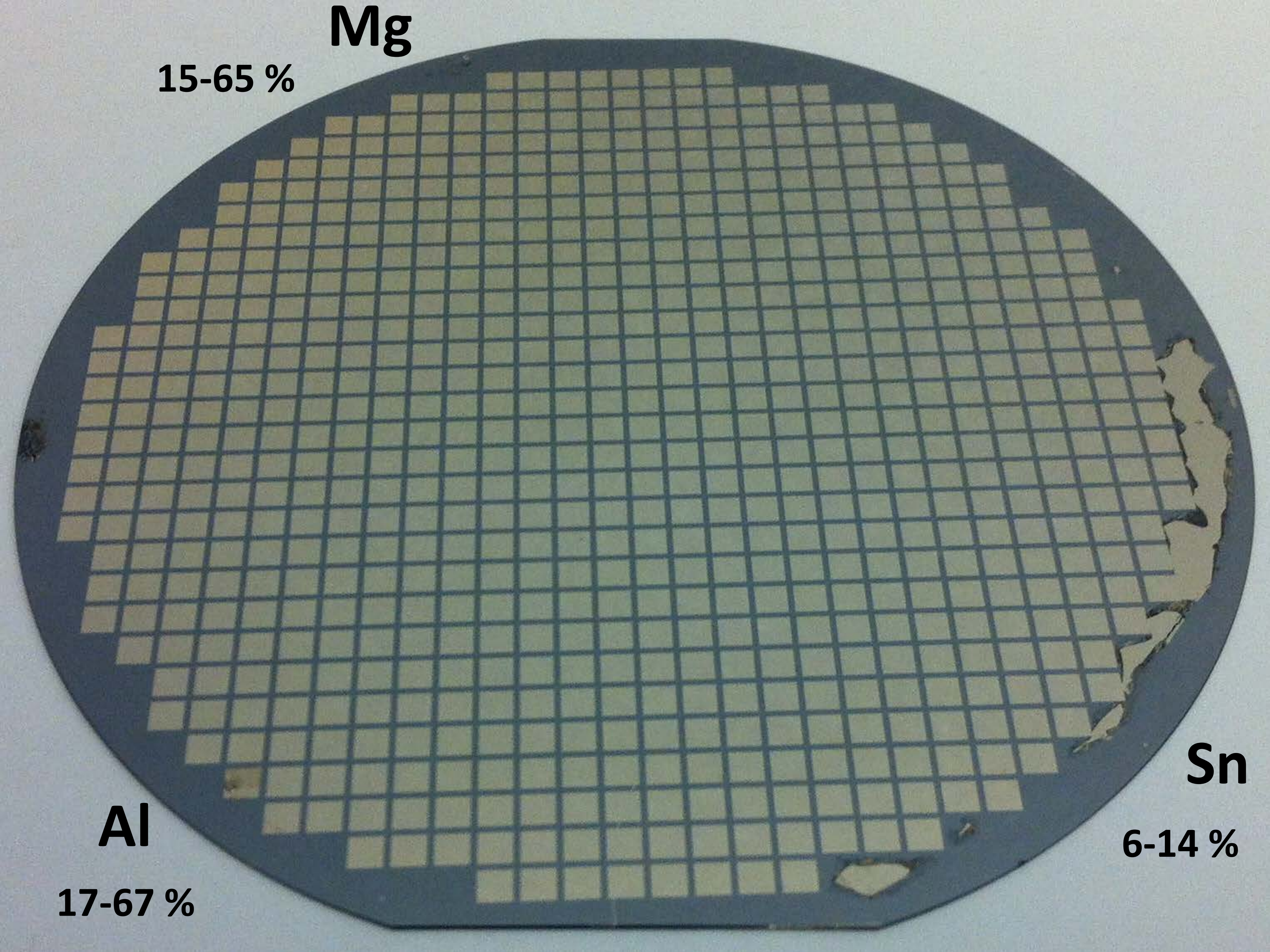
**Primary phase**

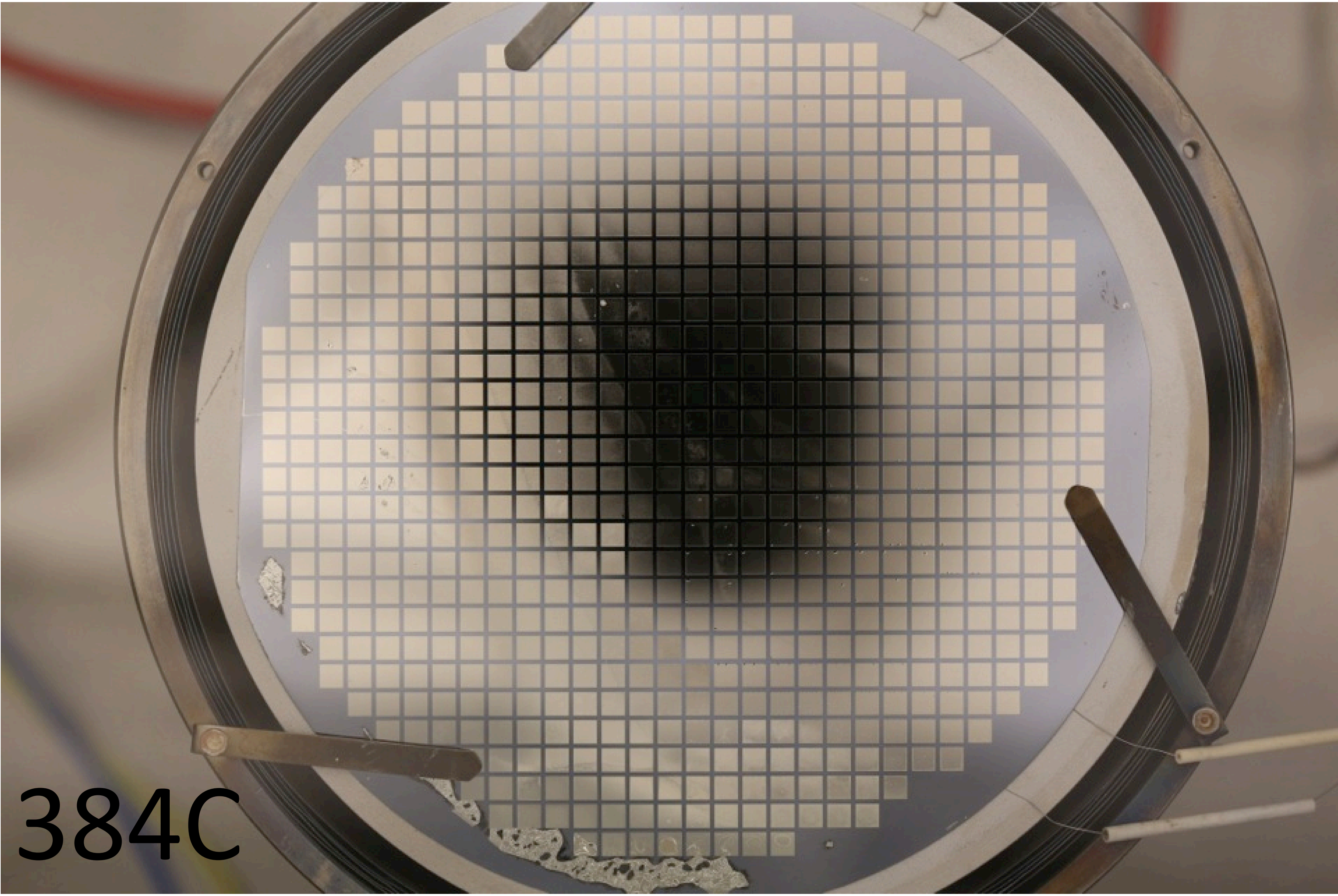


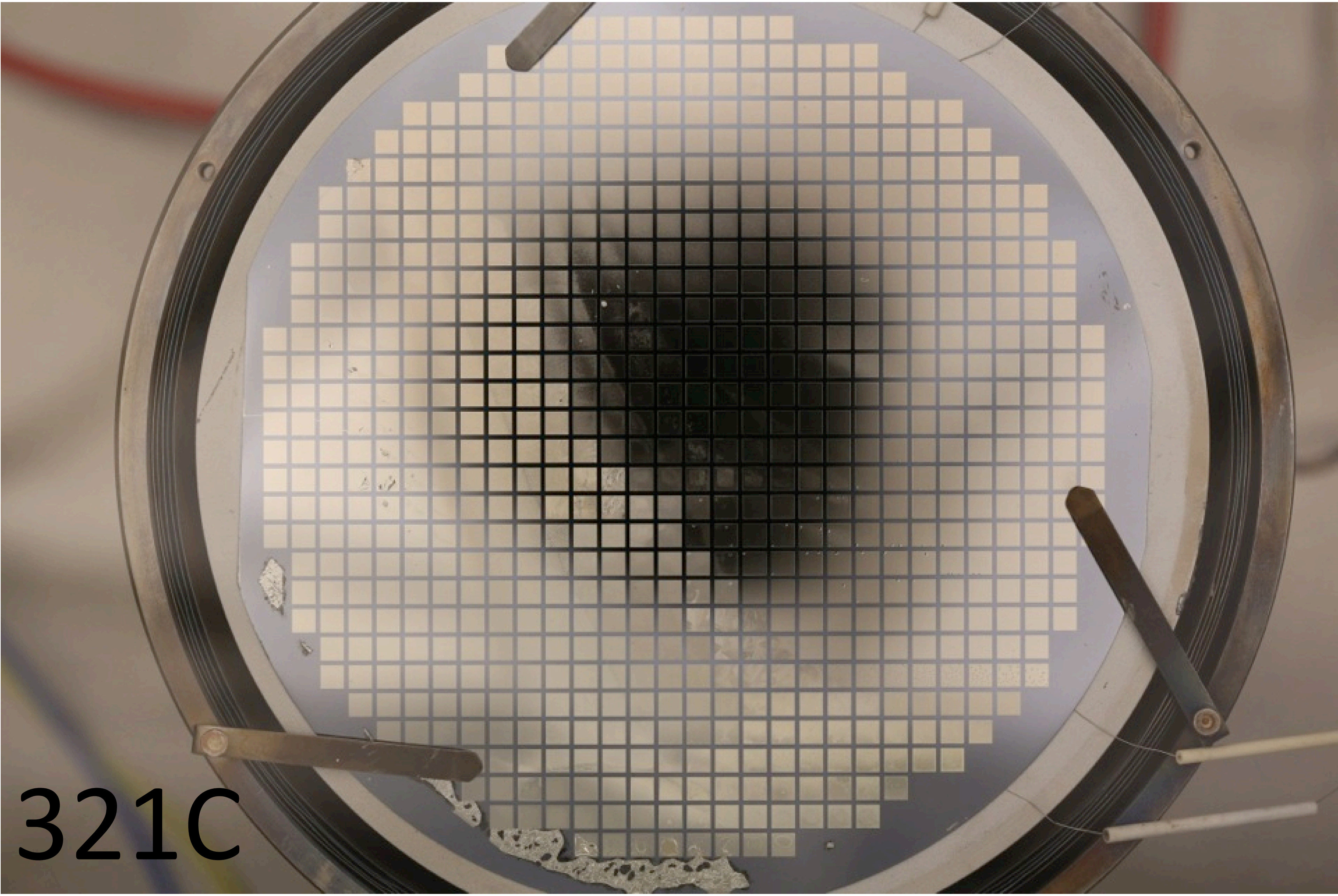

**$T_N$**



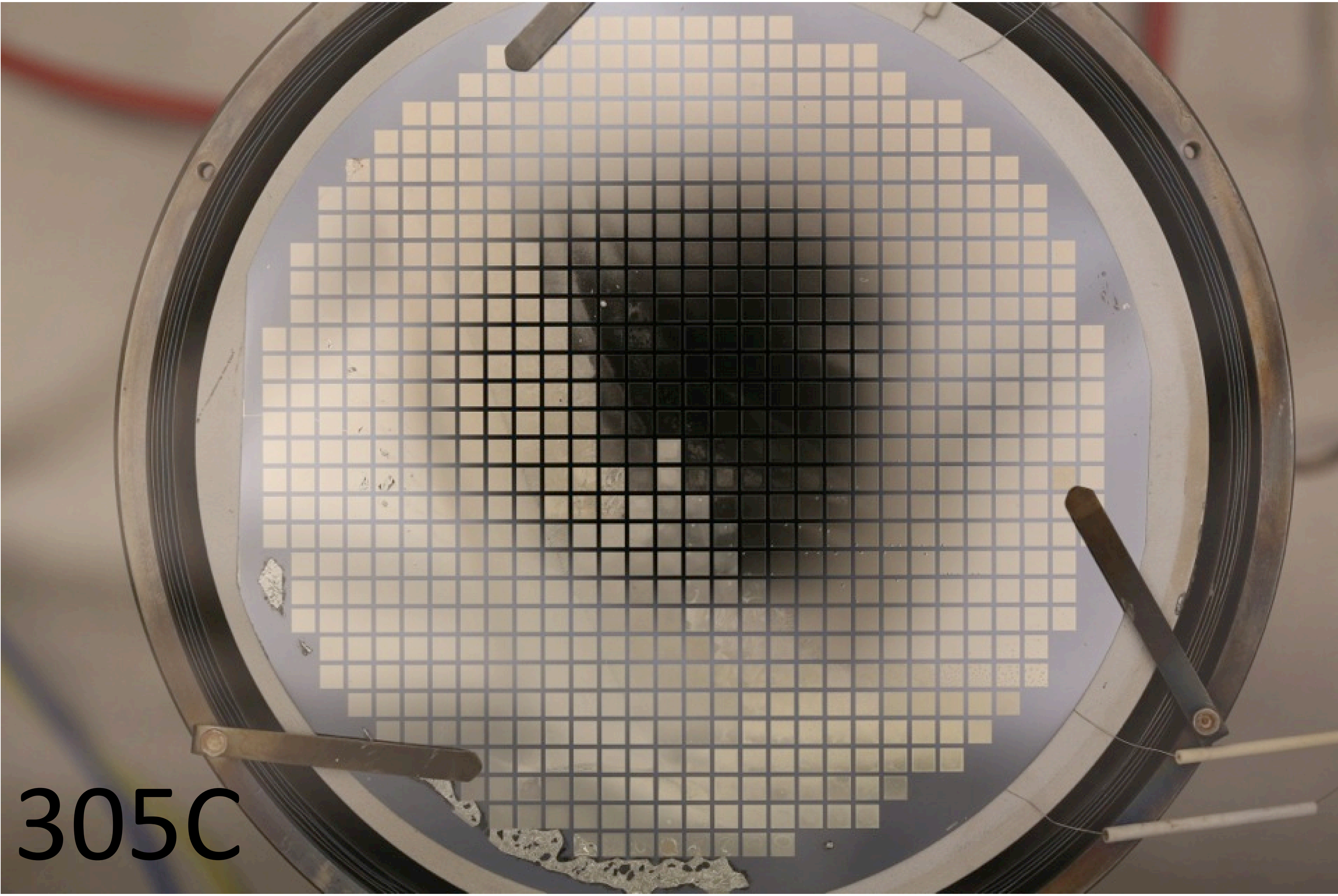

**Insight in glass formation, nucleation (c)**
**Identify new glass formers**

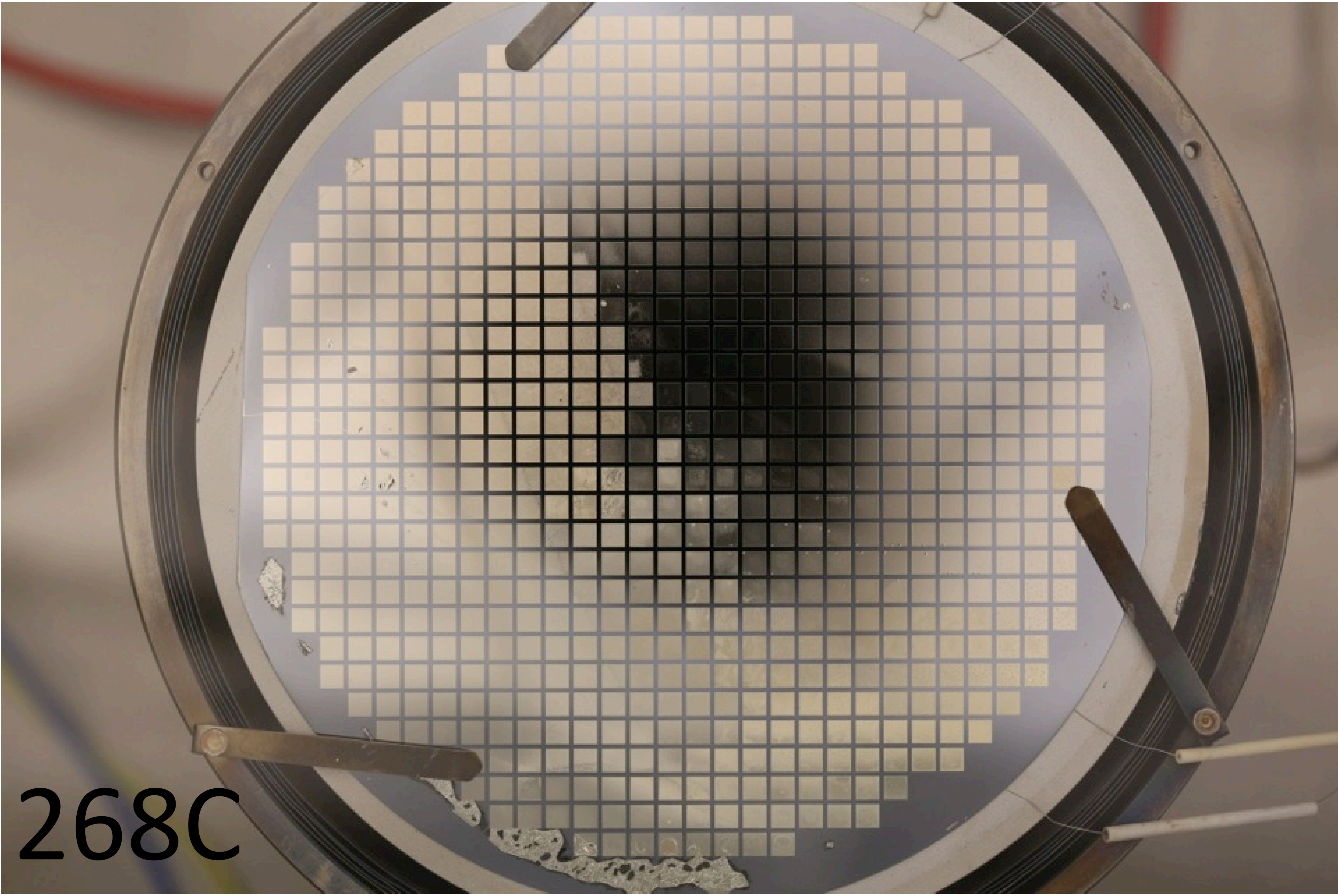

Mg
15-65 %
Al
17-67 %
Sn
6-14 %


384C

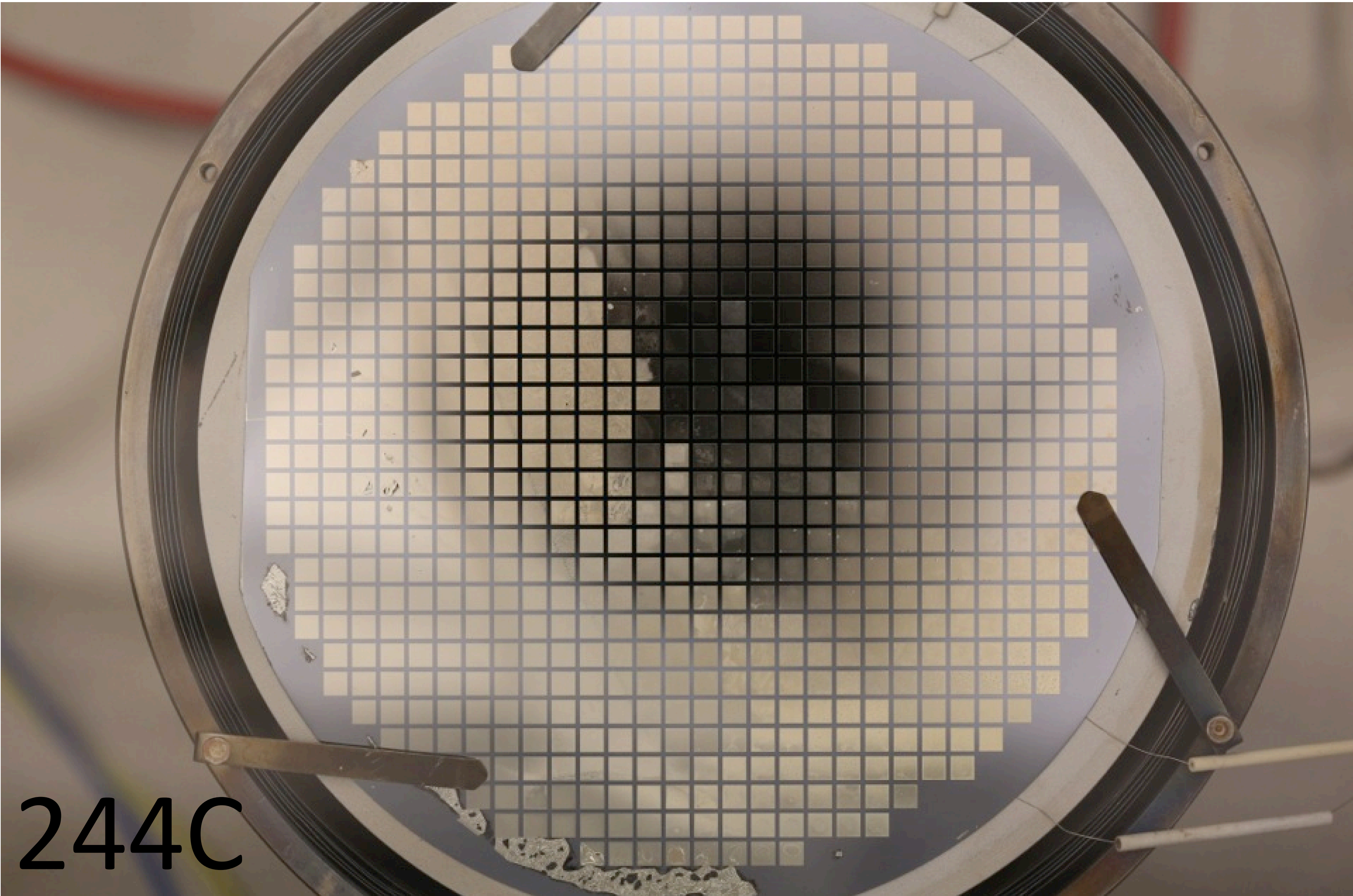


321C

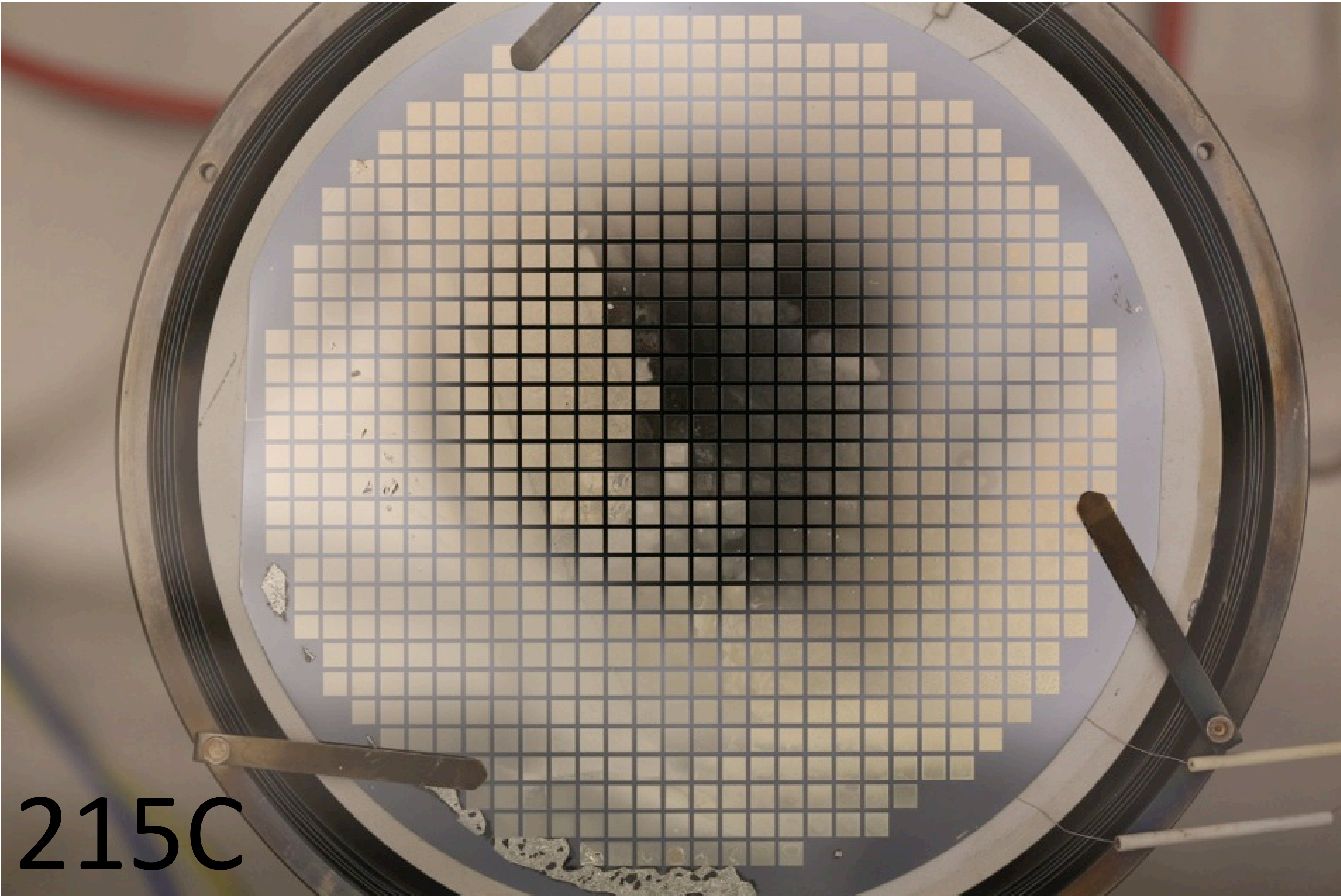

305C



268C

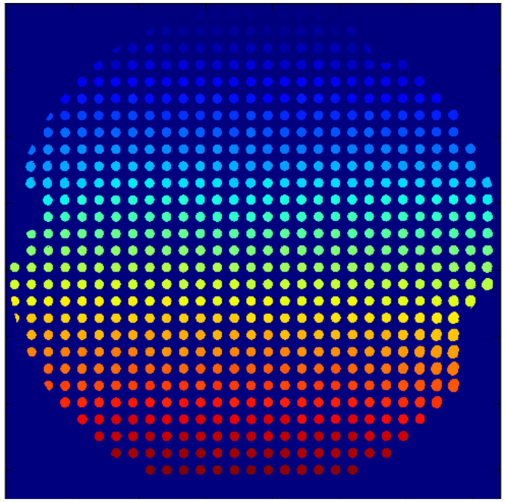


244C

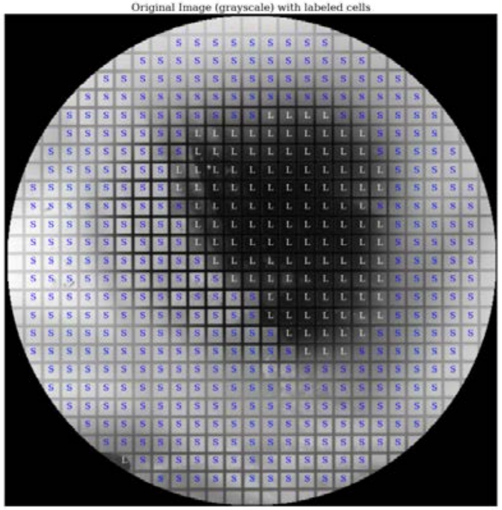

215C

# Automated Image Analysis for High-Throughput Liquidus-Temperature Screening

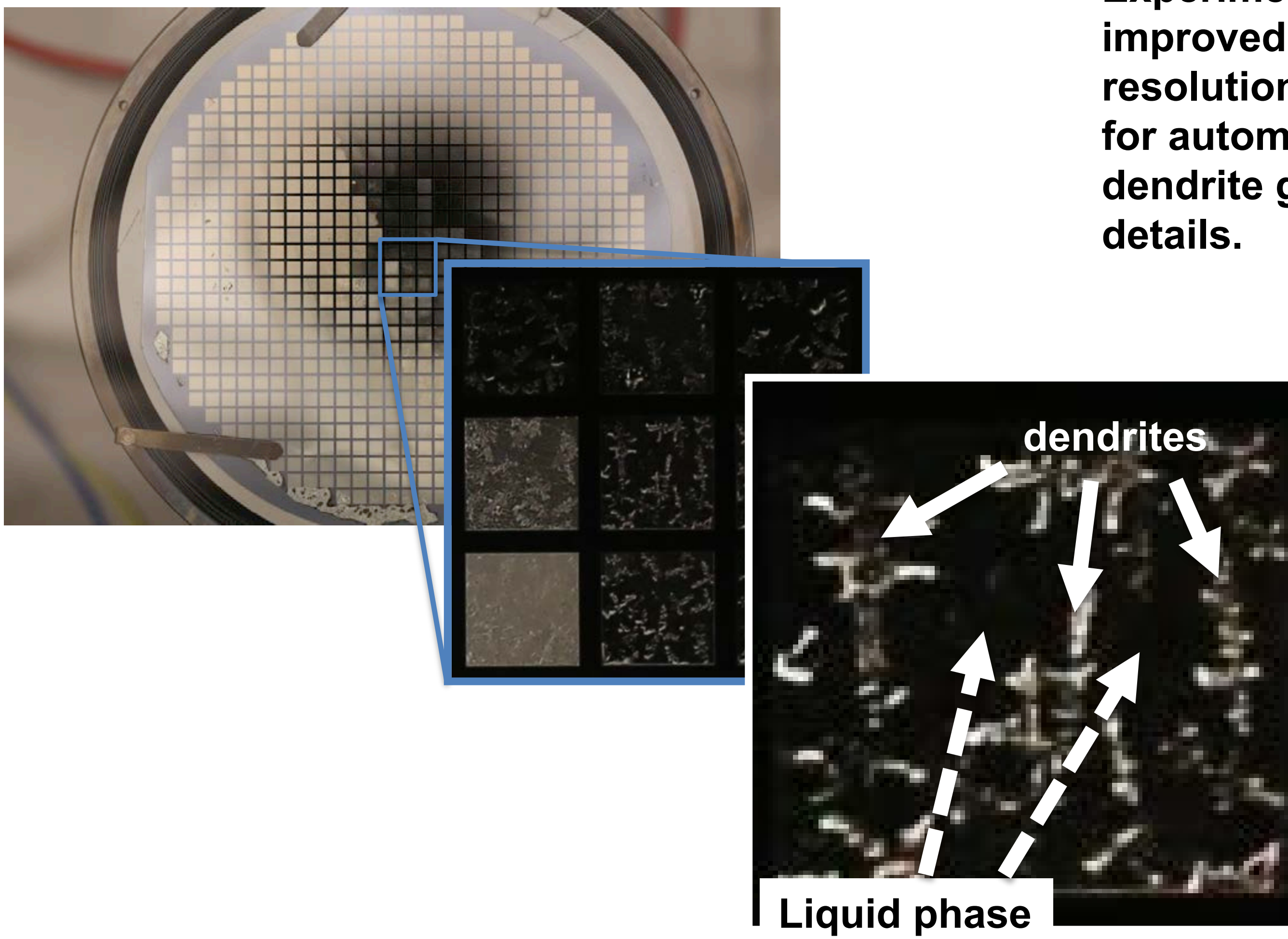
- Different compositions mapped onto a wafer in a regular pattern.
- Solid/liquid transitions identified through changes in the optical images of the cells.
- Image processing software automates the analysis of the cells
  - Image cropping, thresholding
  - Labeling of all cells
    - The cells identified independent of their shape and size
    - The grayscale value of all pixels in the cell is averaged and used to help classify the cell as solid or liquid
  - Automation over many frames as a function of time and temperature



Original Image (grayscale) with labeled cells



# Image Analysis: Complications

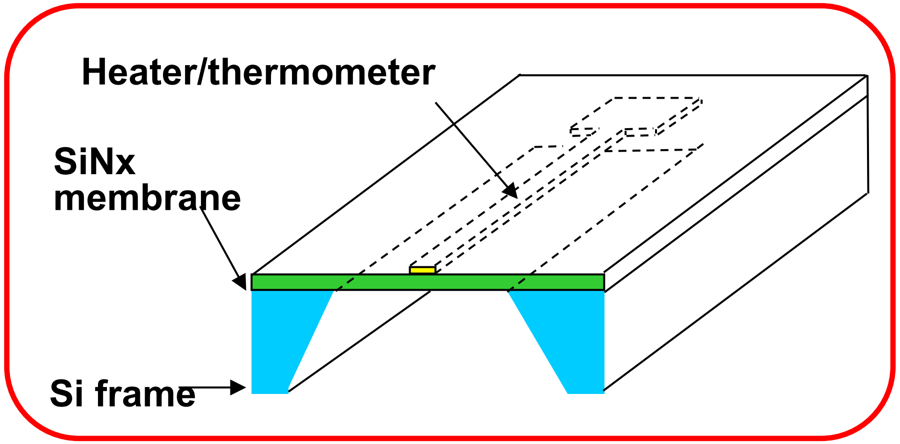


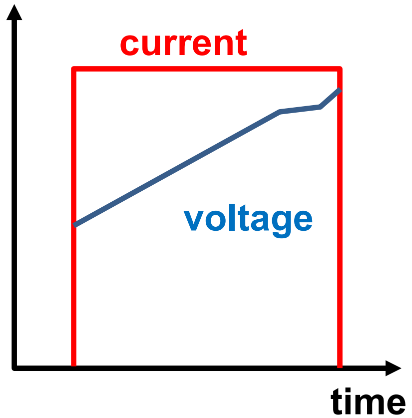

**Experimental setup is being improved for high resolution optical imaging for automated analyses of dendrite growth and other details.**

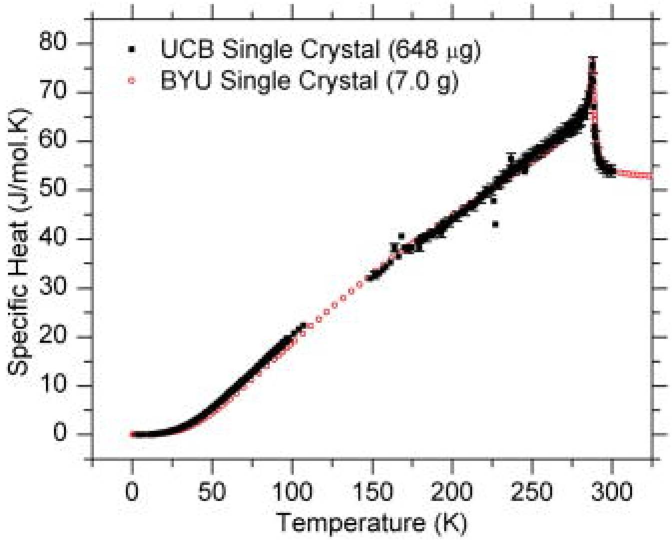
# Nanocalorimetry

**Rapid measurements of the melting point and heat capacity of thin films.**

**Complements and validates massively parallel optical estimation of melting points.**

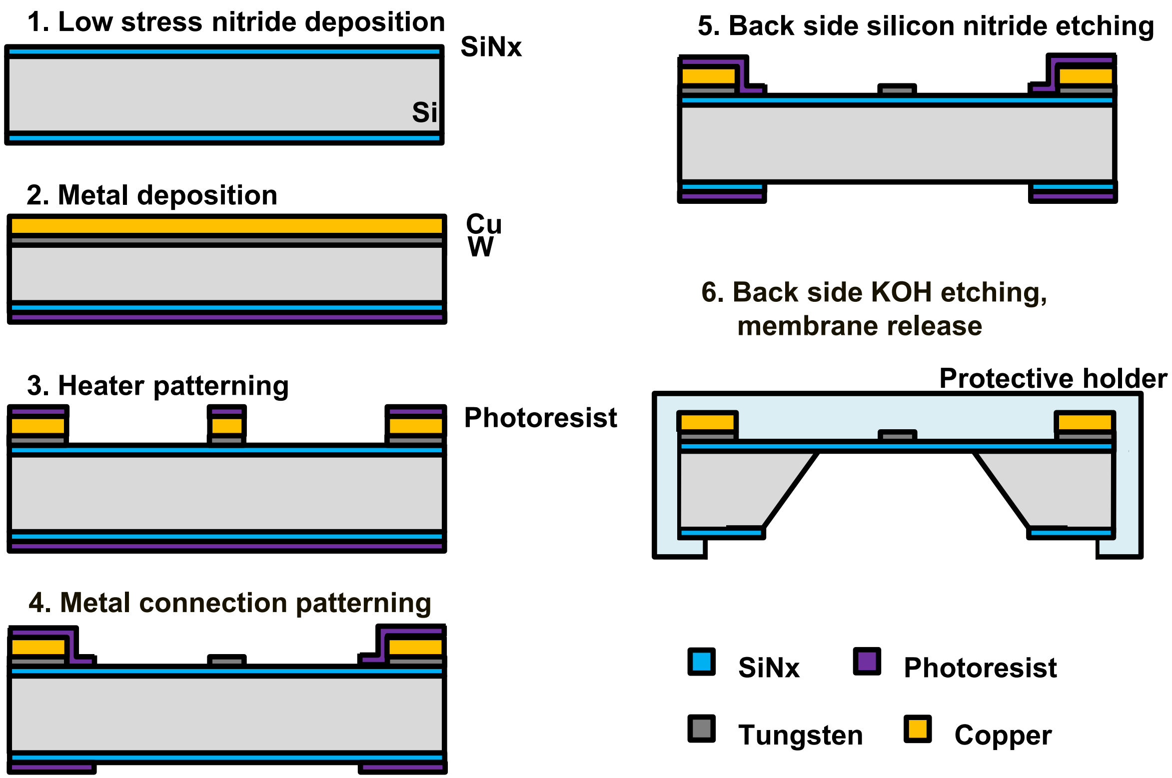


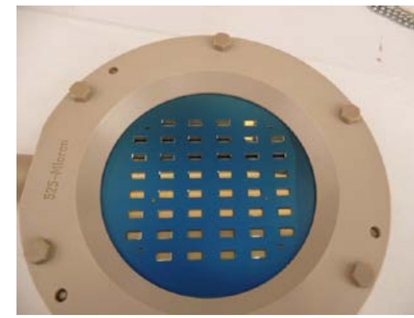



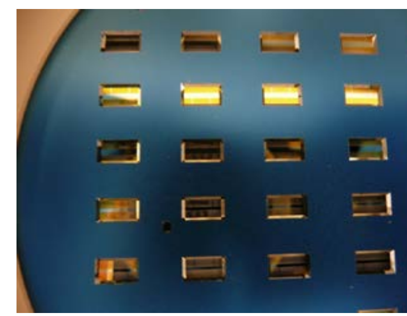



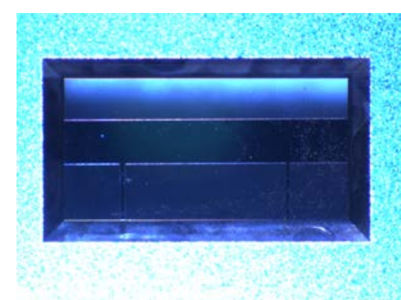

(Cooke et al., *Rev Sci Instrum,* 2008)

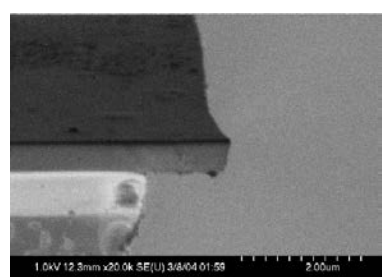
# Fabrication of Nanocalorimeter Array









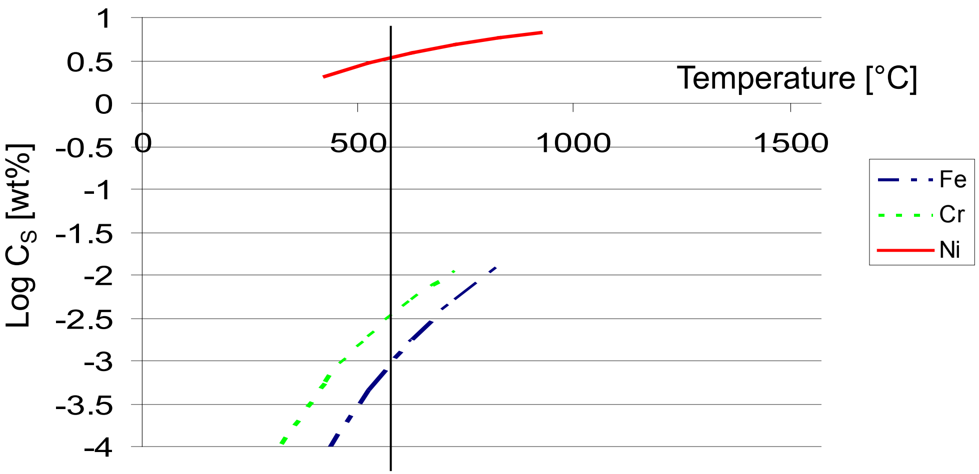
SEM image of the SiNx membrane of thickness ~ 100 nm

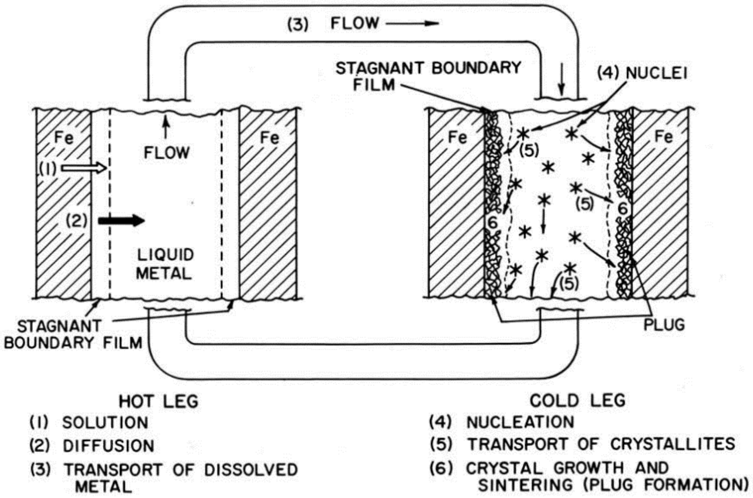
# Corrosion of Structural Materials by Liquid Metals

**Fe in LBE (200 hours at 450°C)**

**In a flow loop system, simply relying on the saturation of corrosion products does not work!**

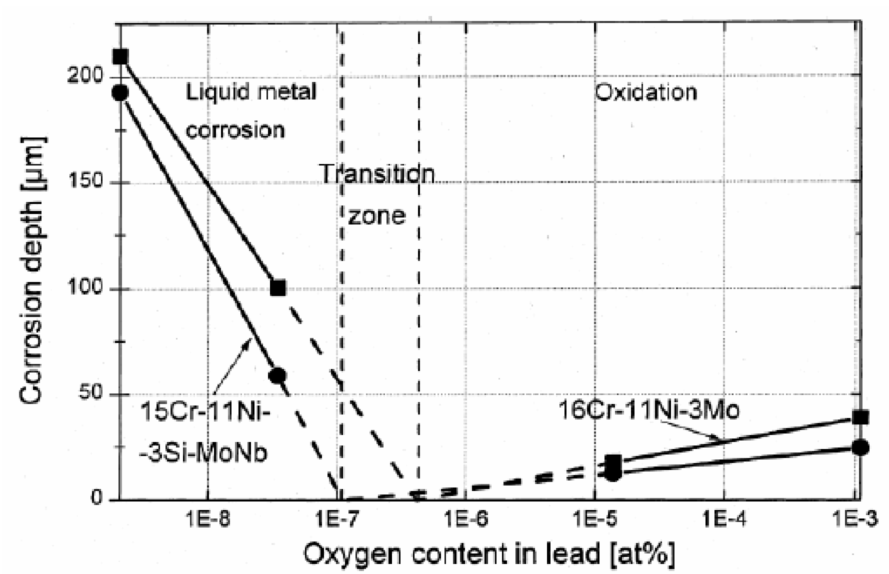
**Temperature Dependent Solubility of Ni, Cr, Fe in LBE**

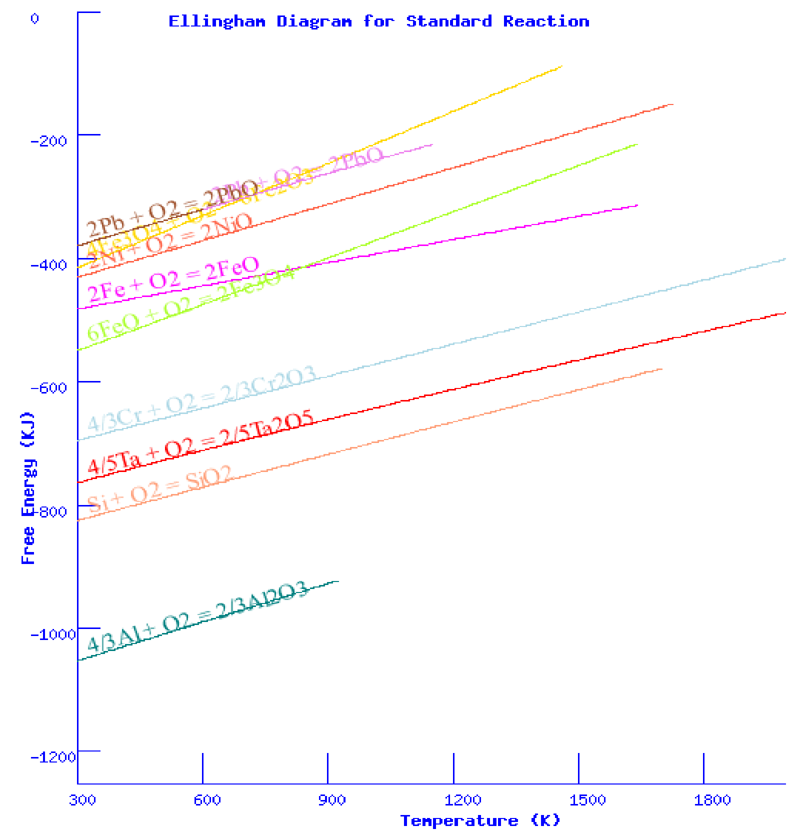


# Corrosion Mitigation Strategy based on Passivation Layer Formation

## Oxygen control to mitigate corrosion in LBE

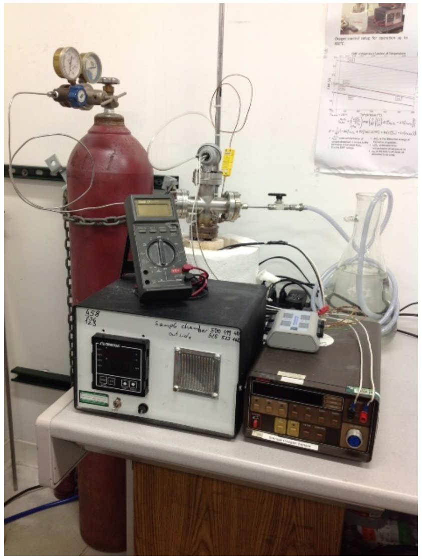



## Extension through thermochemical modeling

# Corrosion and Creep Testing Setup

**Static corrosion testing setup**

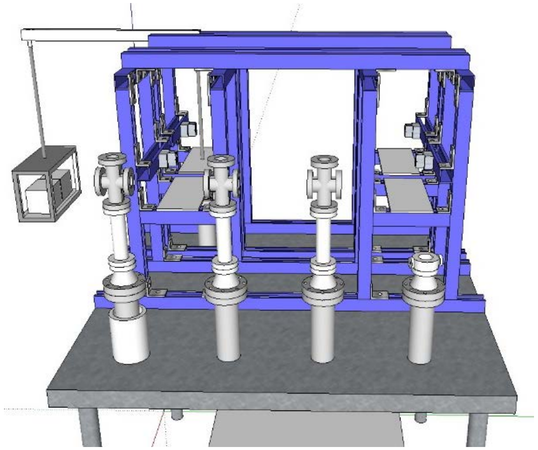


**Can reach up to 1100 °C**

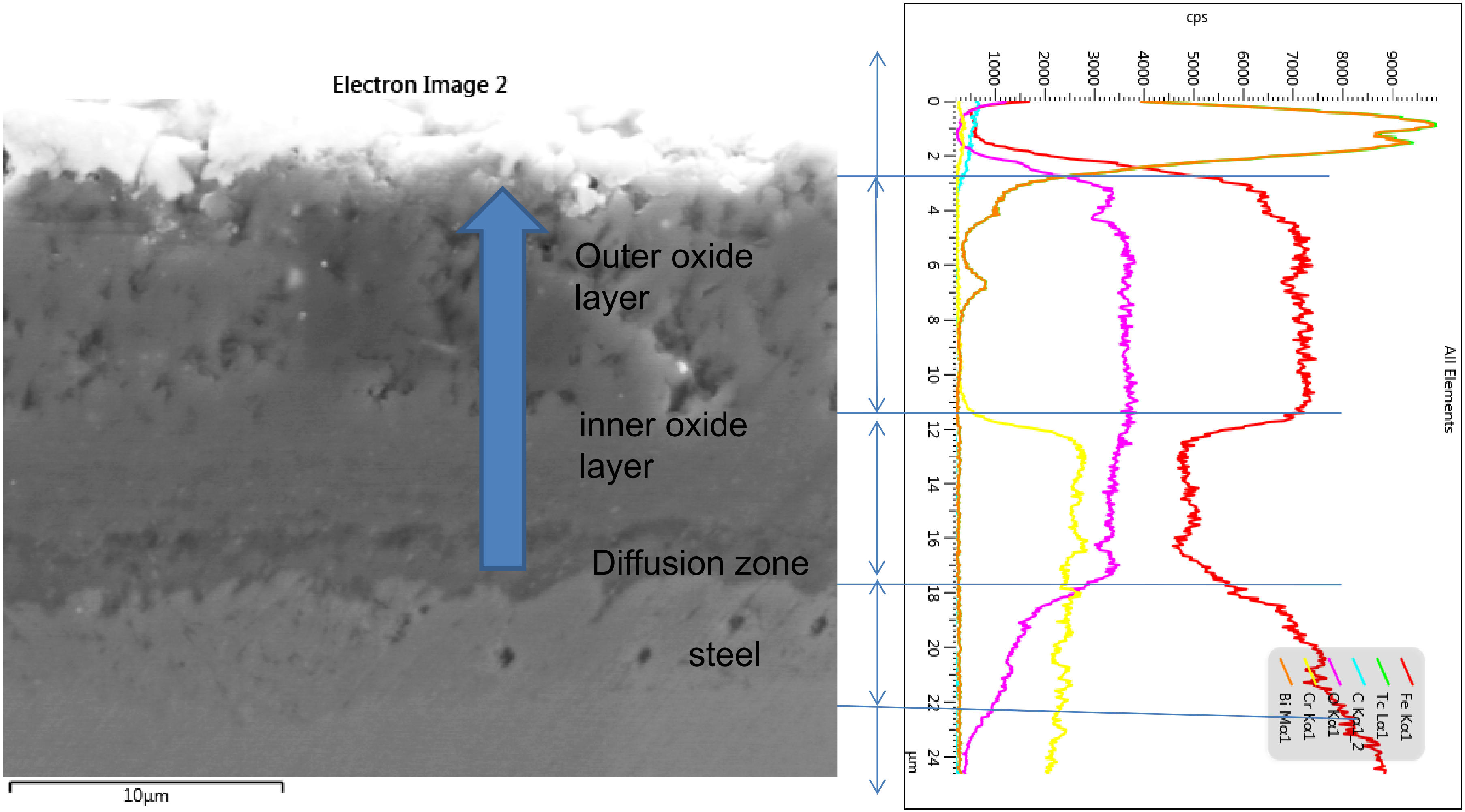
**Measure and control oxygen content**

**Automated data acquisition to measure over long periods of time**

**Creep Testing Setup**

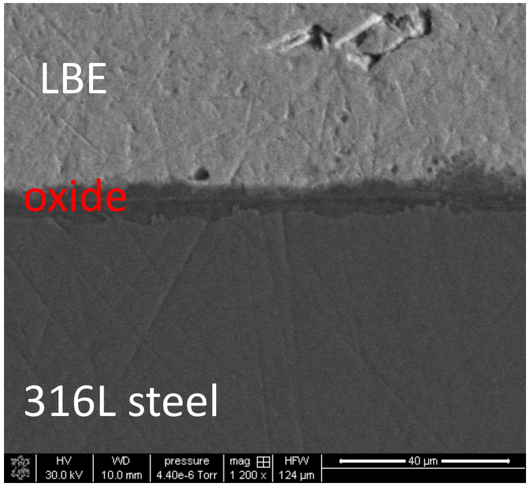


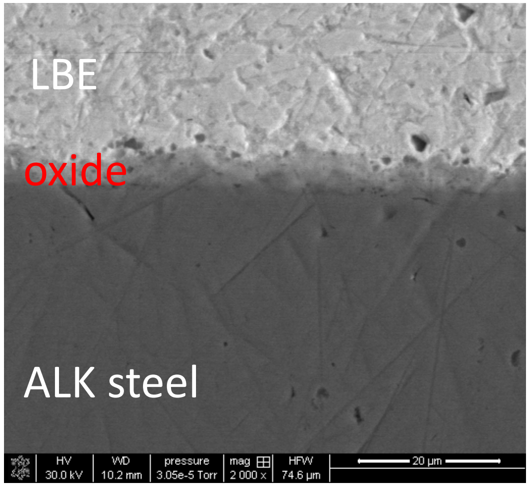
# Detailed Study of Passivation Layer Growth

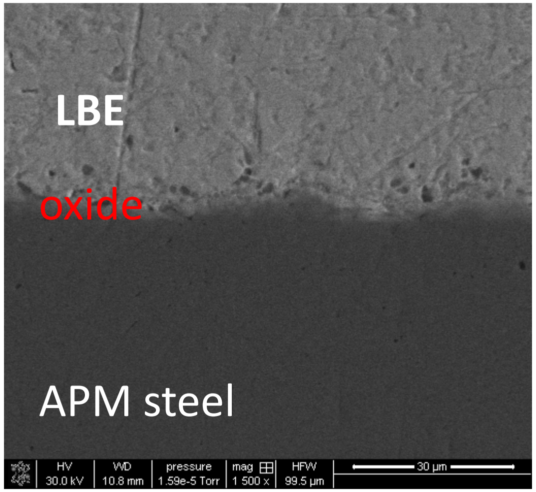


# Passivation Layer Growth for LBE (Pb-Bi Eutectic): Substrate Effects - Preliminary Results

**90 hours**

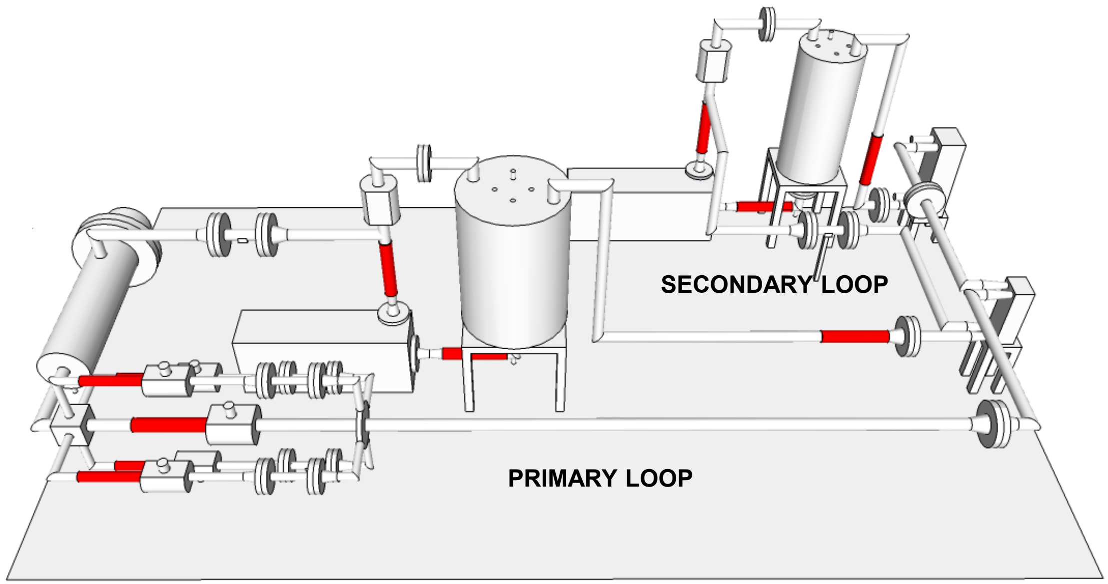



**316L steel chemical composition: 16-18% Cr, 10-14% Ni**
**ALK steel chemical composition: 14-16% Cr, 4.3% Al**
**APM steel chemical composition: 20-23% Cr, 5.8% Al**

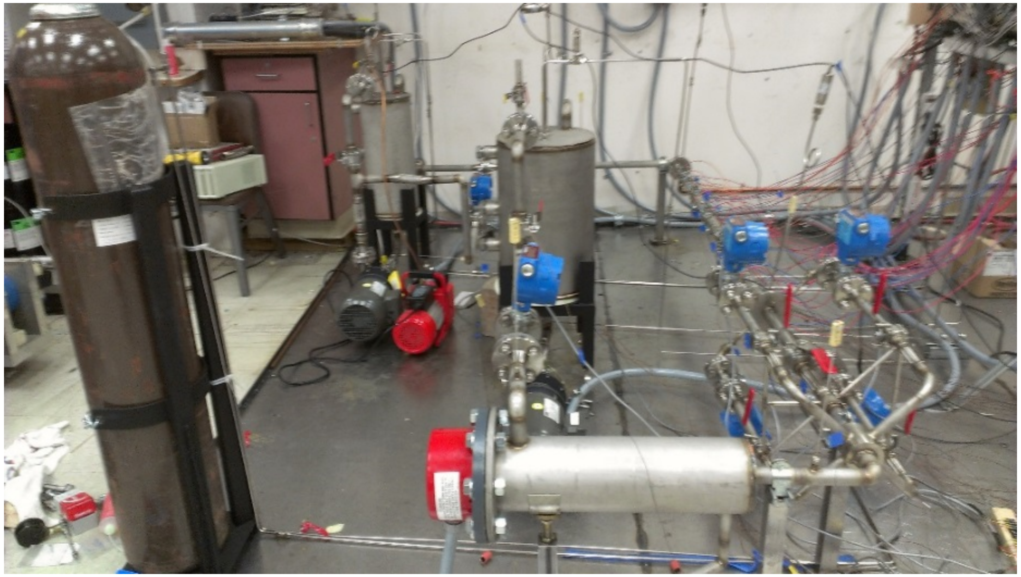
# Flow Loops for Corrosion/Heat Transfer Characterization




- ❖ A "medium"-temperature loop with Dowtherm A has been constructed as a test bed for later high temperature (> 800 °C) loops for corrosion, erosion and heat transfer studies.

- ❖ This loop will also act as an intermediate heat exchange loop (i.e., provide the cooling circuit for the high temperature loop).

# Flow Loops for Corrosion/Heat Transfer Characterization



- **Design Operating Conditions:**
  - **Inlet liquid temperature: 25 – 300 °C**
  - **Test section power: 0.5 – 8 kW**
  - **Preheater power: 12 kW**
  - **Reynolds number: 5000 – 50,000**
  - **Prandtl number: 4.6 – 43**
  - **Experiments with and without tangential injection swirl enhancement**

# Summary/Future Plans

- ❖ We have established capability to synthesize and rapidly screen combinatorial libraries of liquid metal alloys and are applying this capability to identify promising compositional spaces.

- ❖ We are establishing capability to validate/iteratively improve computational thermodynamics modeling to help guide the experimental efforts.

- ❖ We have developed and constructed static corrosion and creep testing setup and validated their operations.

- ❖ We have designed and are constructing a "medium"-temperature flow loop as a test bed for later high-temperature loops and also for use as an intermediate heat exchange loop.

  We are currently completing the loop construction and will begin baseline heat transfer experiments to evaluate heat transfer enhancement schemes.