SAND2013-9659C

Energy Systems Development at Sandia

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Sandia National Laboratories, CA

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Outline

- **Sandia's energy missions and core competencies**
- **Subject of presentation**
  - ✓ Hydrogen energy: Structure materials for H-storage
  - ✓ Power source: System engineering of thermoelectric (TE) module
- **Summary**

Sandia National Laboratories

"Exceptional service in the national interest"

- Largest national lab, focus more on engineering & applications
- Missions
  - Energy and climate
  - Nuclear security engineering
  - Defense systems
  - Homeland security
- Locations
  - Albuquerque
  - Livermore
  - Also Nevada, Hawaii, DC

Energy Security

Energy, Climate, & Infrastructure Security (ECIS) SMU Program Areas

Energy	Climate	Infrastructure	Enabling Capabilities
Margie Tatro Deputy: Andrew Orrell	Rob Leland Deputy: Marianne Walck	Len Napolitano Deputy: Pablo Garcia	Charles Barbour Deputy: Jerry Simmons
Renewables Juan Torres			very mons
Nuclear Andrew Orrell			nalysis ur (Interim)
Transportation Bob Carling			and Policy ur (Interim)
Efficiency Jerry Simmons	Ray E. Finley	Jeff Danneels	A-E Wahid Hermina

Mission

To accelerate the development of transformative energy solutions that will enhance the nation's security and economic prosperity.

Last Updated 6/5/2012

Energy-related core competencies at Sandia

- ✓ **Fuel combustion**
- ✓ **Hydrogen energy**
- ✓ **Power source development**

Today's discussions

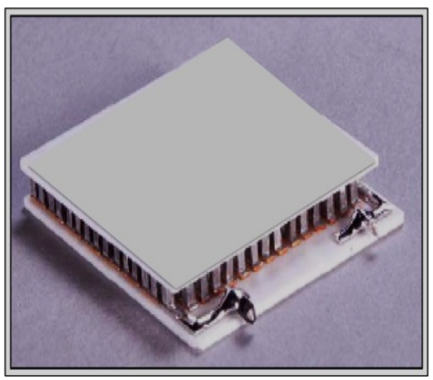
Programmatic Goals and S&T Engagements

Develop Materials and Capabilities

Enabling design and build

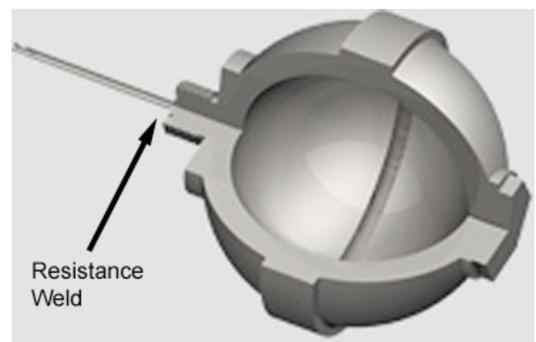
Reliable High Performance Energy Systems for Defense or Commercial Use

Thermoelectric Module



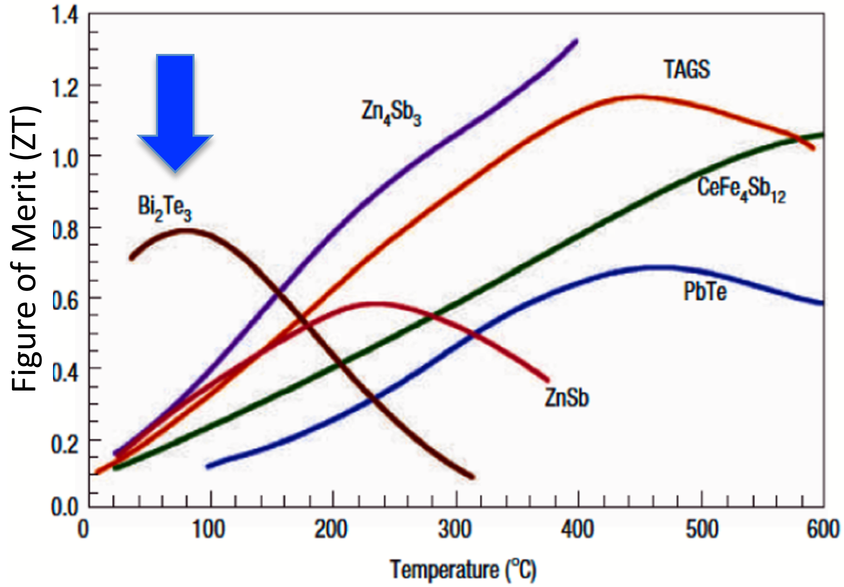
Design/construct thermoelectric module to mine power from low level heat source

Structure for H2-Reservorr



Design and construct a reliable hydrogen storage reservoir

Thermoelectric fundamentals and system selection



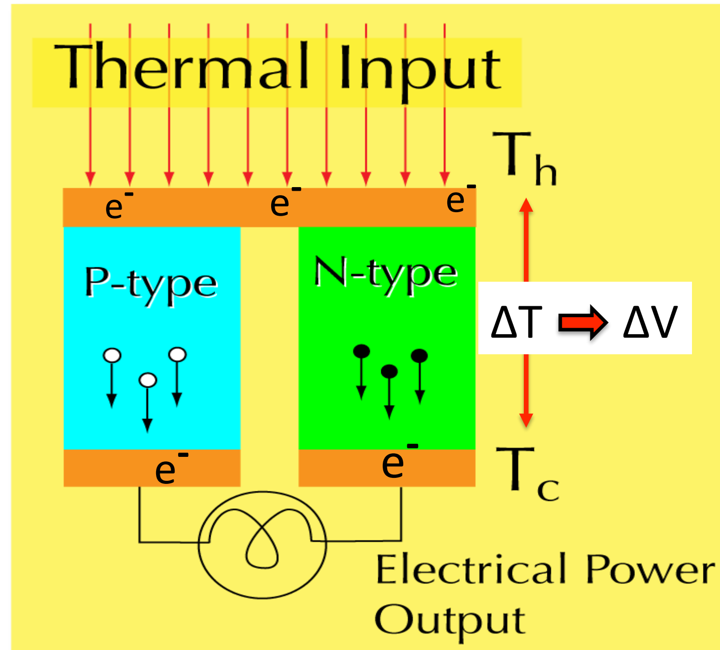
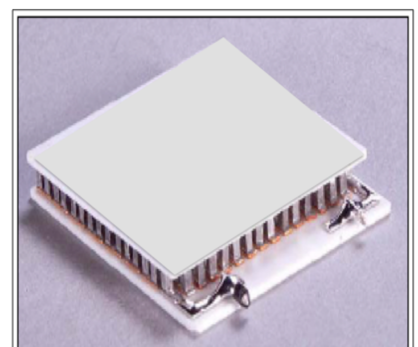


Figure-of-merit: $$ZT = \frac{S^2}{\rho\kappa}T$$

Typical TE module configuration



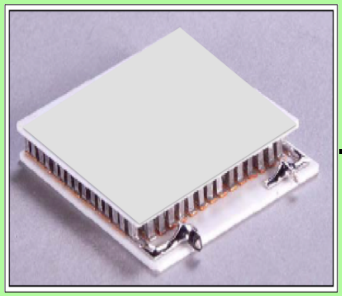
S: Seebeck's coefficient
ρ: Electrical resistivity
K: Thermal conductivity

Experimentally measured

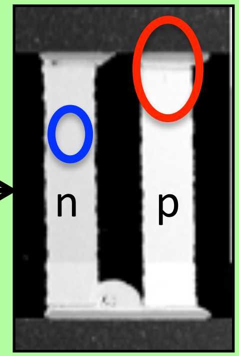
Generator Efficiency : $$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1+ZT_{avg}} - 1}{\sqrt{1+ZT_{avg}} + T_c / T_h}$$

Material factors associated with Bi_2Te_3-based TE module design/construction

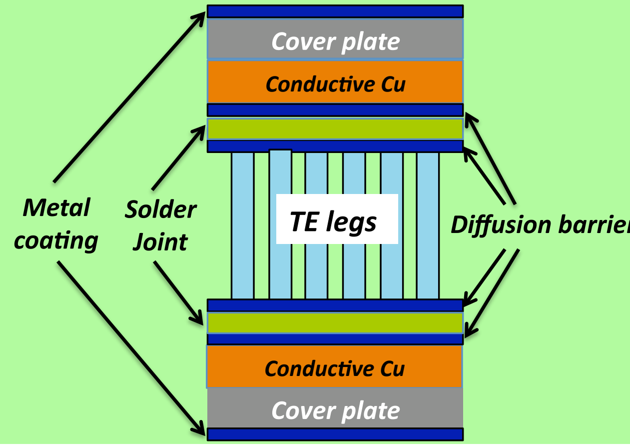
Typical design/construction of Bi_2Te_3-based TE module



Cross section



Schematic of construction



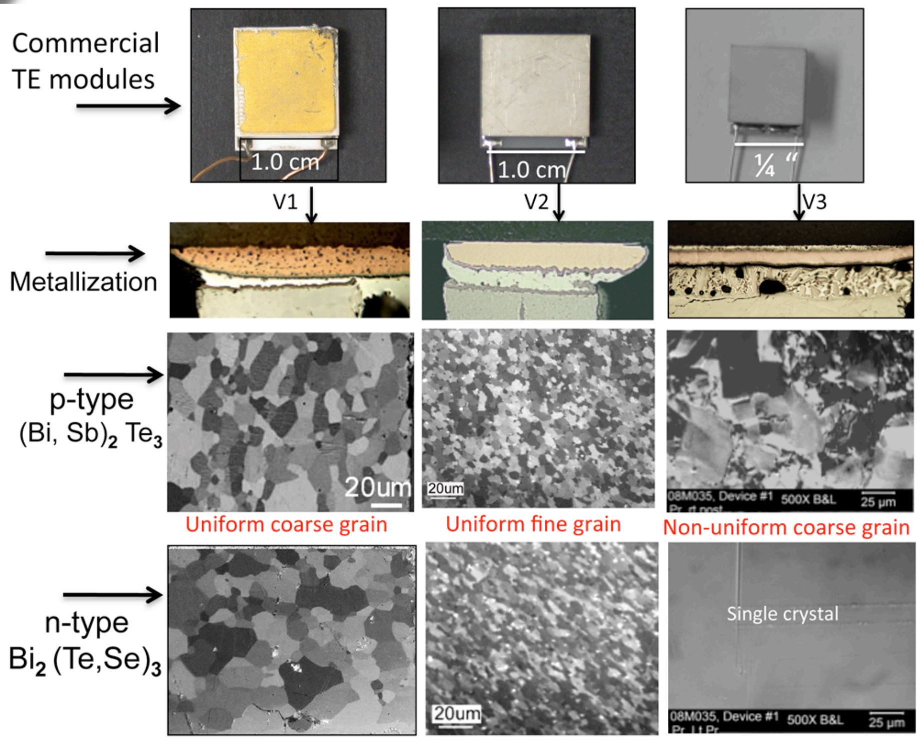
Bi2Te3-based alloys

- p-n alloys synthesis & processing
- Alloy metallurgy & thermal aging
- TE transport property
- Mechanical behavior

Module/ Device

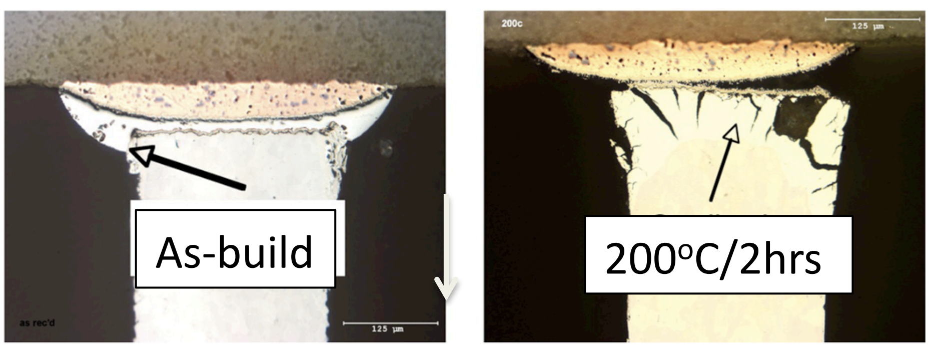
- Contact-metallization design & fabrication
- Material compatibility/thermal aging
- Contact metallization's resistance
- Material-device interaction & structure integrity

Material and System Engineering Challenges of Bi2Te3-based TE Module



Contact metallization design & metallurgy impact structure integrity and system performance

Physical metallurgy of p-n alloys impacts ZT and in turn, power generation efficiency



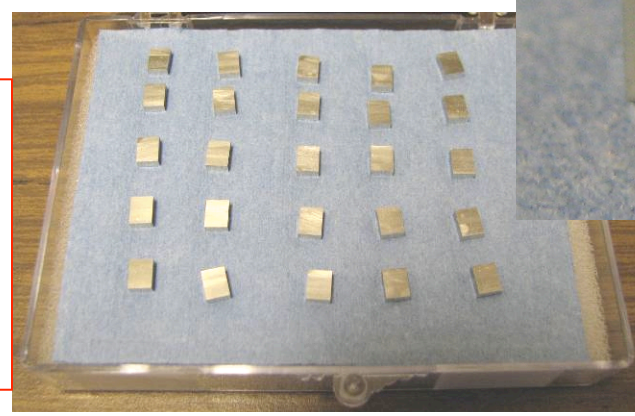
Inadequate material design and construction led to premature failure of the Bi2Te3-based module

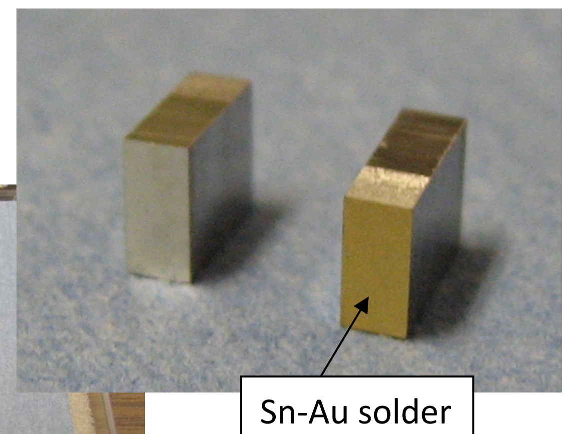
Mitigation and/or engineering solution?

Test matrix for determining the ultimate contact metallization system

Base TE Material	Diffusion Barrier	Solder	Aging Temperature	Aging Period
p-type Bi-Te	Electroless Ni	Sn0.8Au0.2	100 °C	One week
n-type Bi-Te	Electroless Co		175 °C	Three months
	Electrolytic Co		240 °C	Six months
	Electroless Pd			
	Electrolytic Pd			

Electroless cobalt diffusion barrier with 80/20 Au/Sn solder on one end





Reasons for selection:

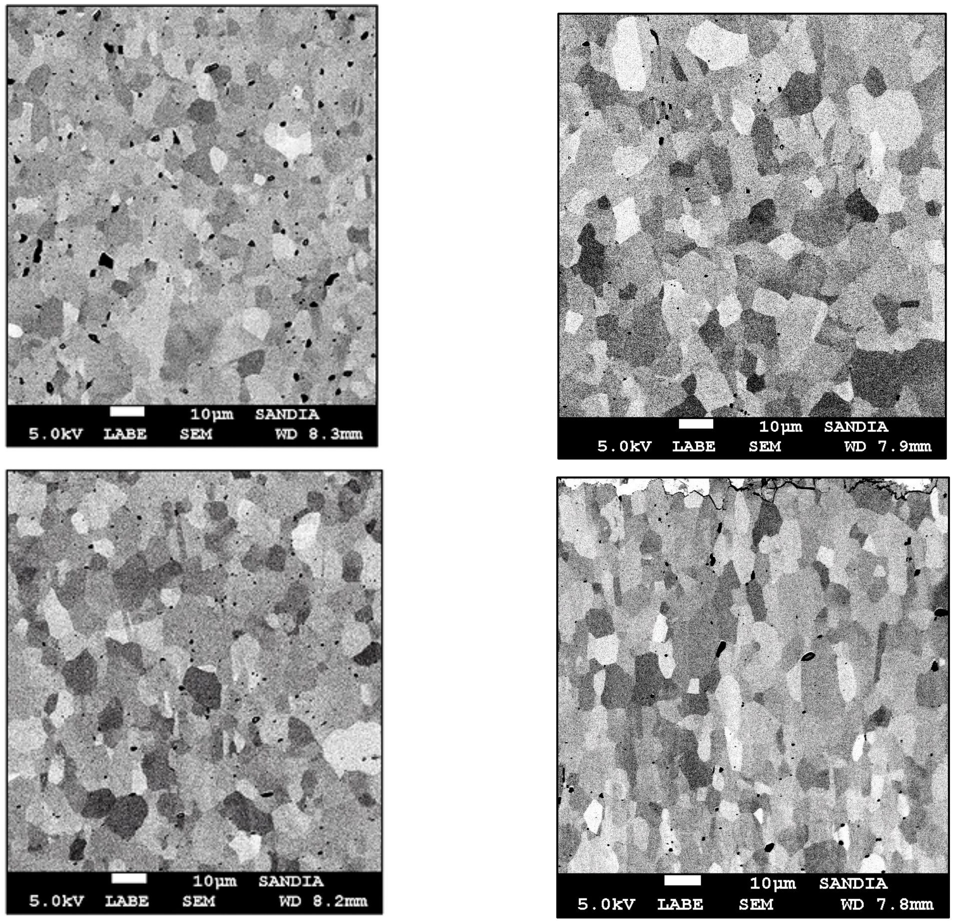
- Compatible coefficient of thermal expansion
- Desirable contact resistance
- Performed at room temperature

Stable Grain Size of p and n Alloys upon Aging Up

As received | 6 month

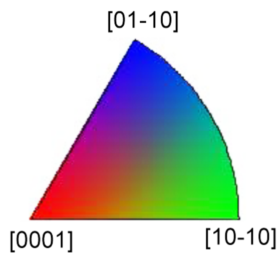
p-type

n-type

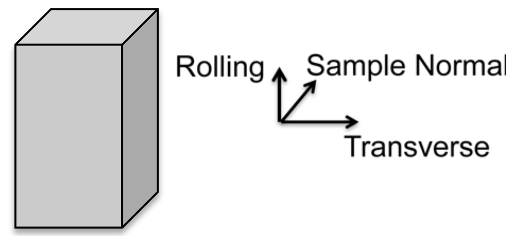


Strong Texture Seen in the p-n base Alloys due to its Rhombohedra Structure

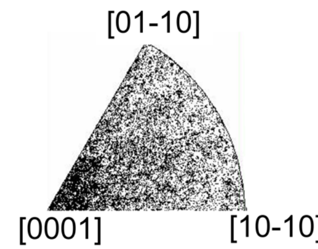
EBSP color map



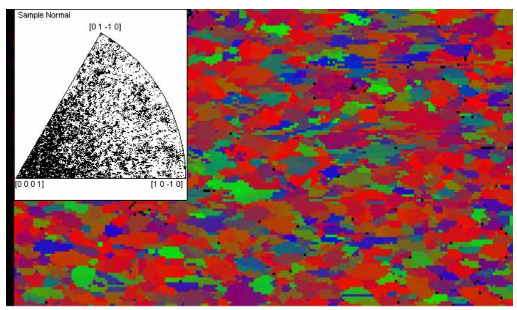
Sample orientation

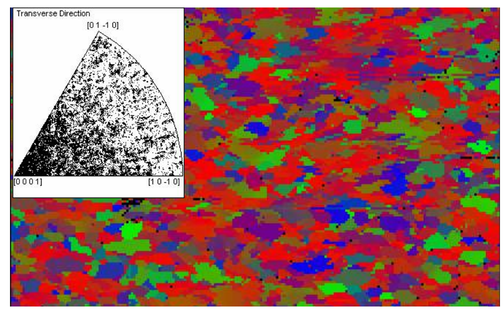


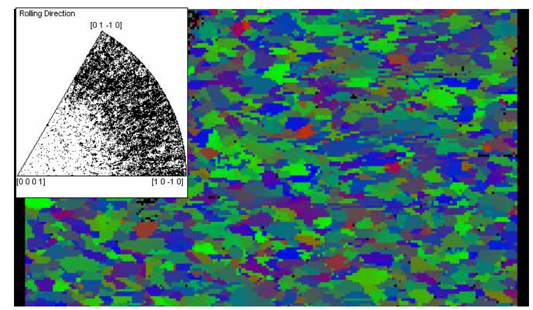
Inverse pole figure



As-received





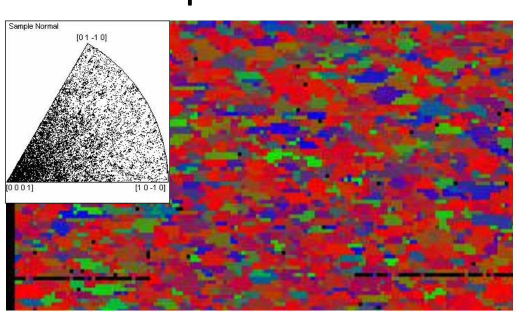


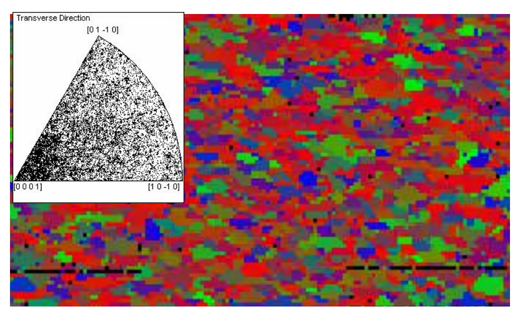
Sample Normal

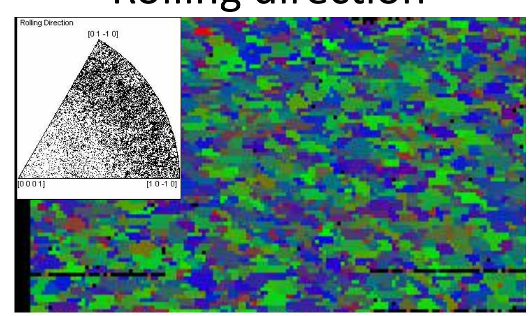
Transverse

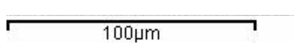
Rolling direction

200°C/2 hrs



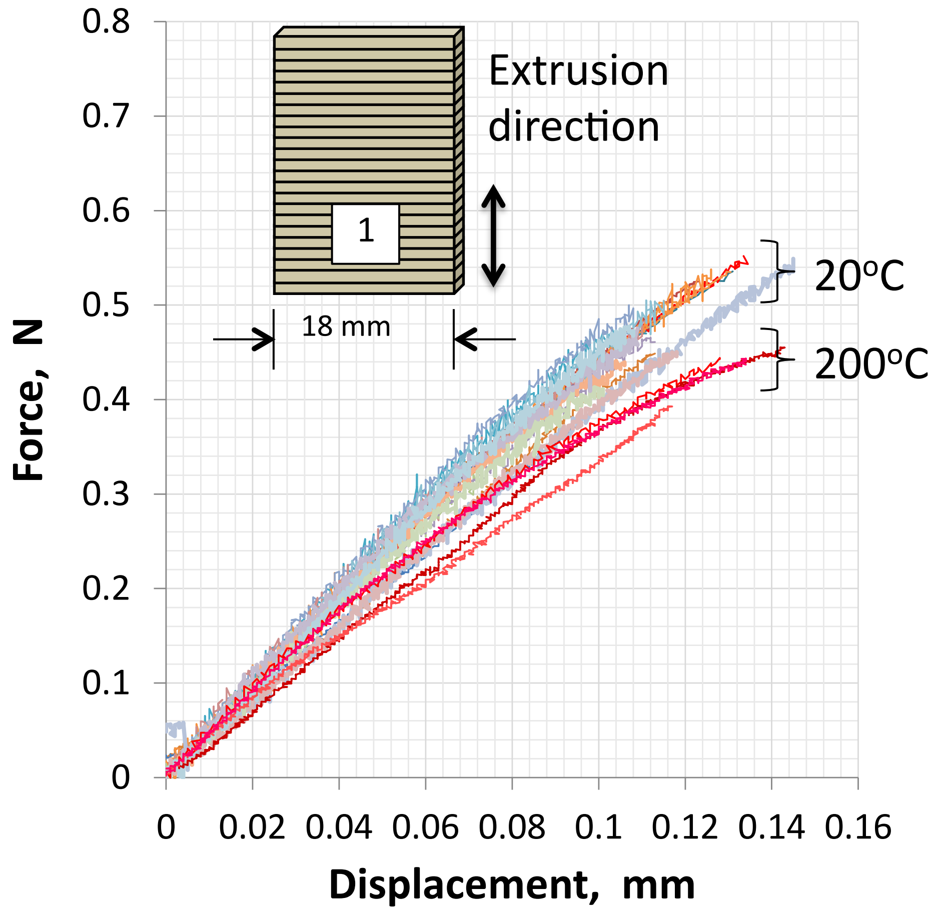




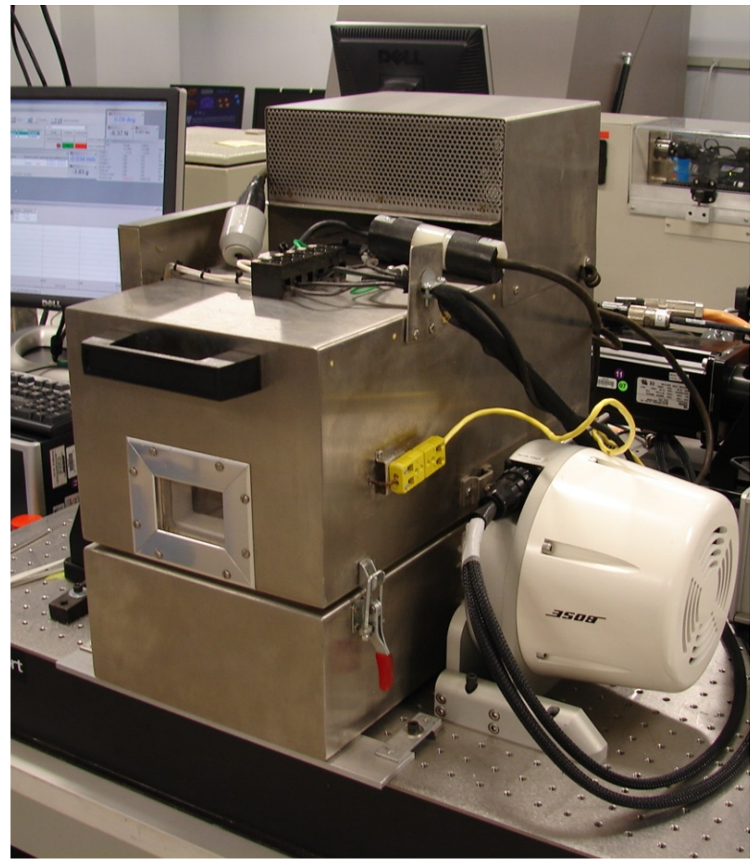


3-point Bend Indicates Slight Drop in strength of n-tile upon 200°C Heating

Bending of N-type Specimens



High temperature 3-point bend tester

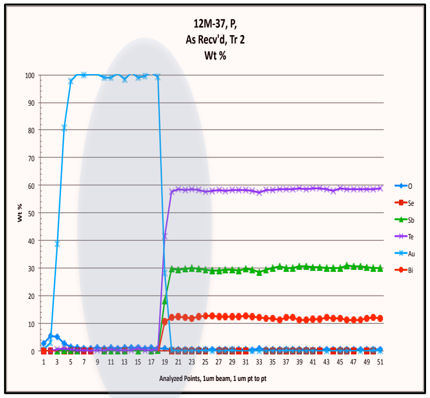


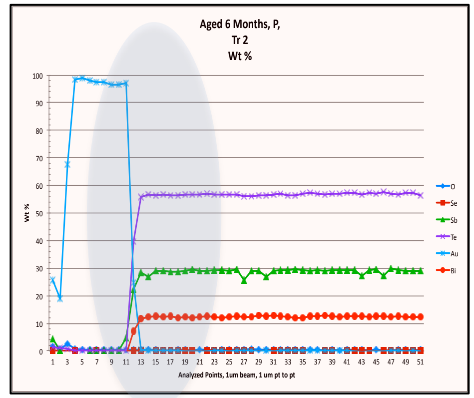
By Wei-Yang Lu, 08256

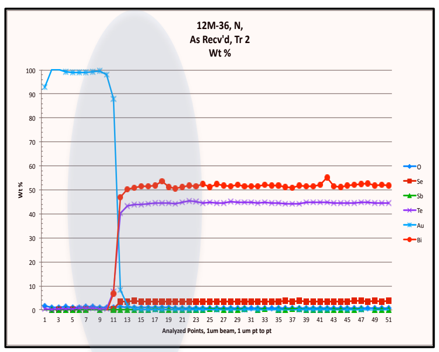
Stable alloy composition with no obvious interfacial reaction upon aging

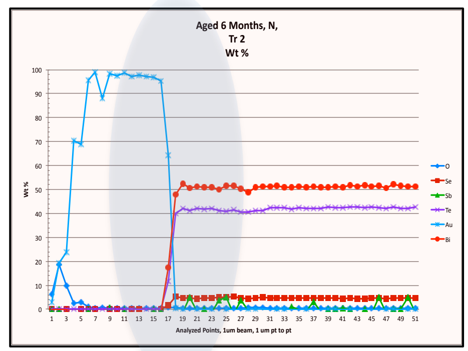
As-received

6 months







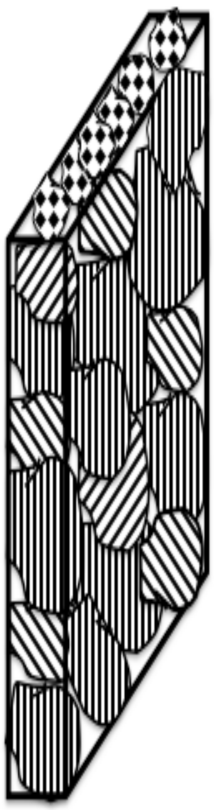


Minor preexisting chemical heterogeneity was also seen in both p- and n- types

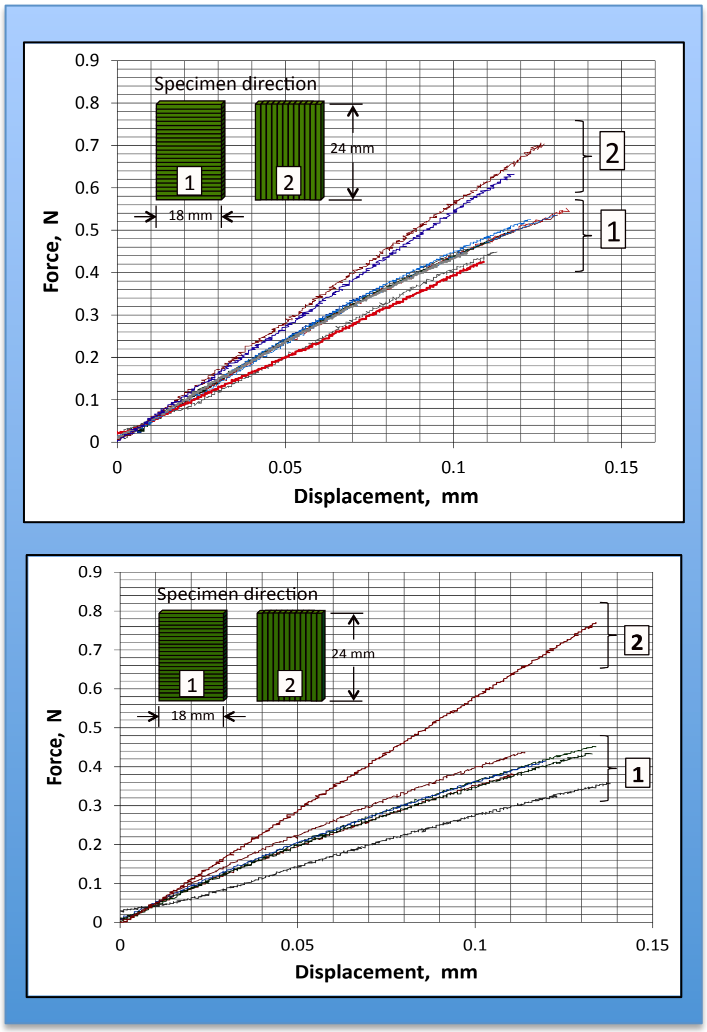
Anisotropic mechanical behavior and TE transport dictate alloy processing & module fabrication/construction

Bend 1: (01-10) out-plane

Bend 2: (0001) in-plane

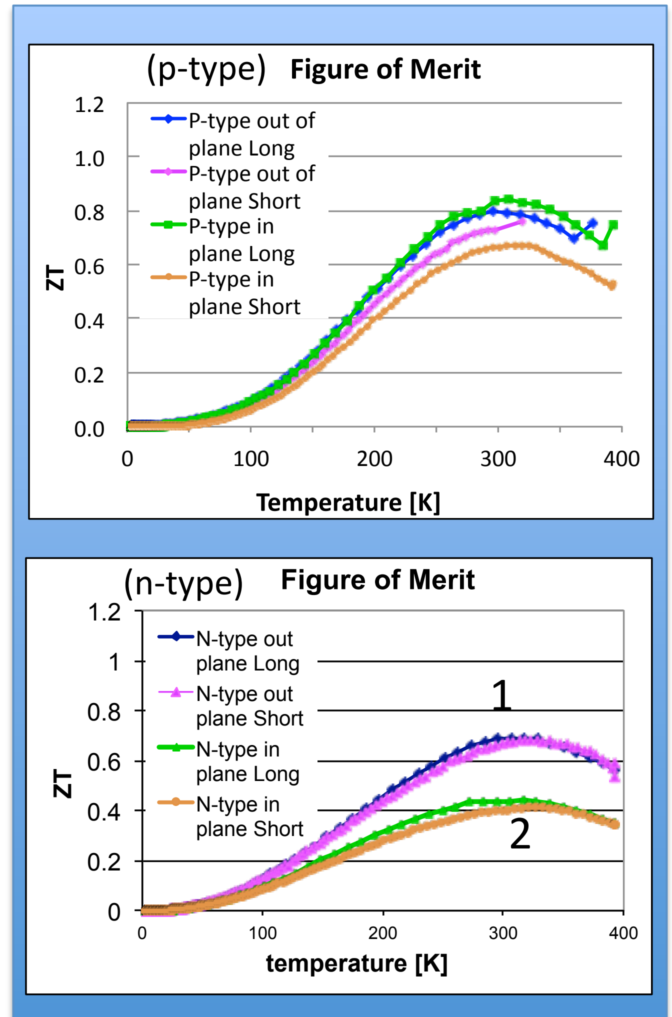


Mechanical strength



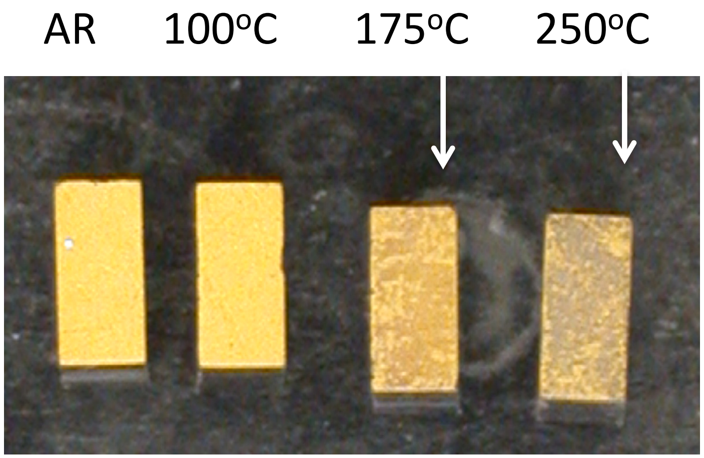
3-point bending by W. Lu

Figure of Merit

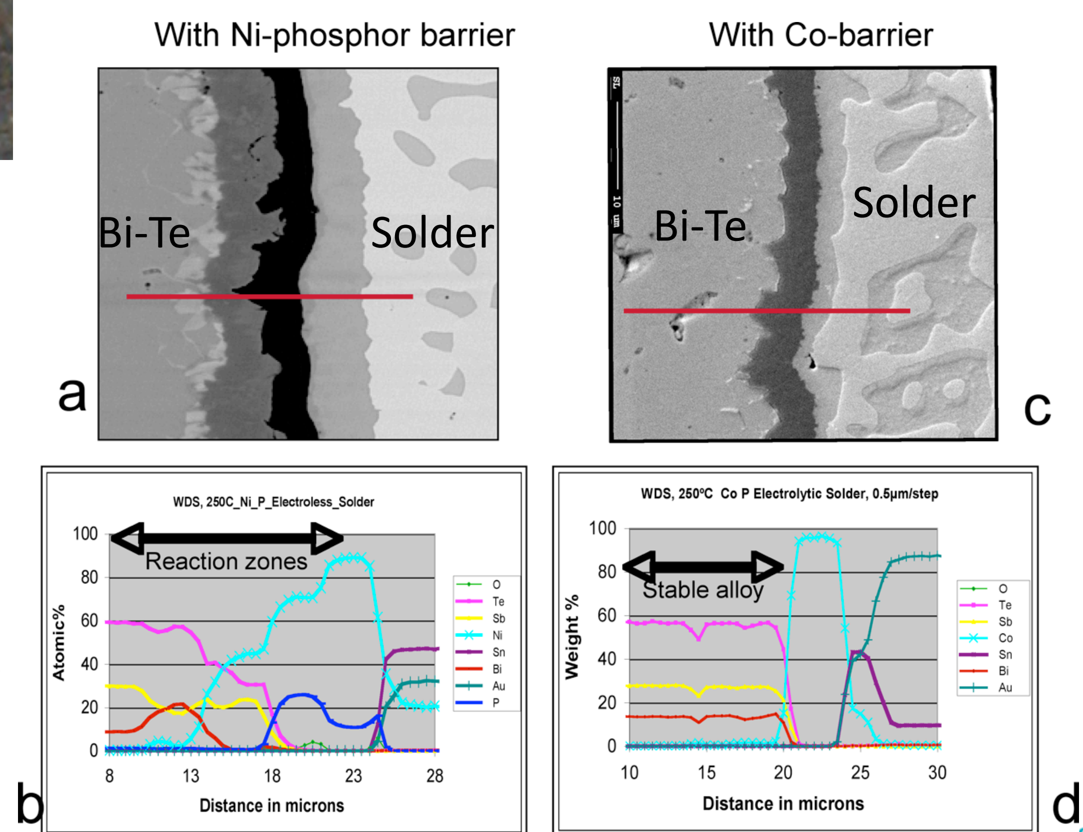


PPMS by N. Nishimoto

Ni or Co with Sn-soldered is eliminated due to metallurgical instability

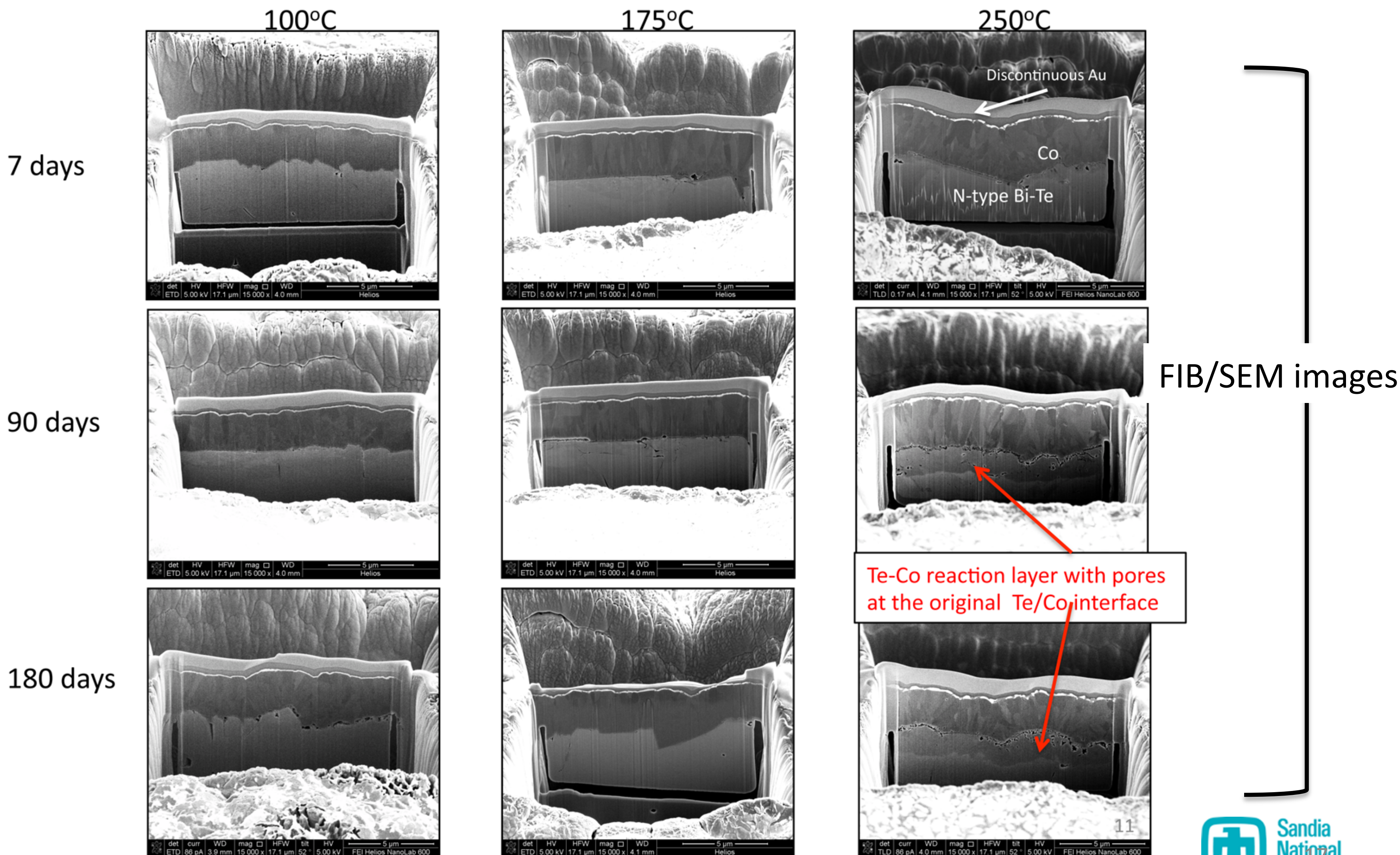


Discoloration on p-pile with Co barrier suggested a metallurgical reaction



Interfacial reaction in p-tile with Ni barrier, at 250°C/7 days.

TEM analysis confirms interfacial instability of metallization with Co barrier

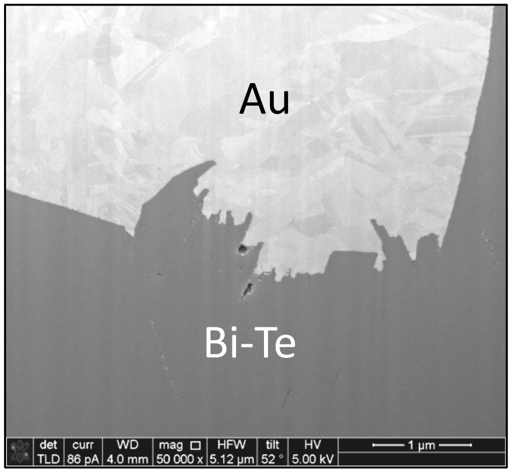


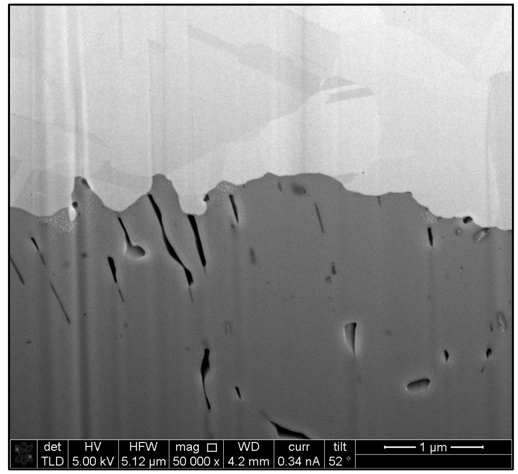
Based on the low solubility of Au in Bi2Te3 and no obvious interfacial reaction, Au/Bi2Te3 is the final selection

AR

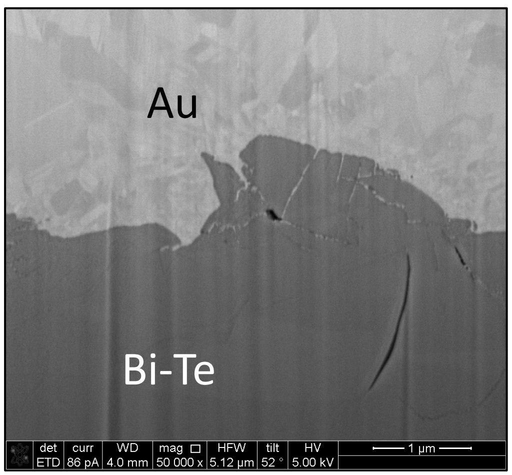
2 weeks

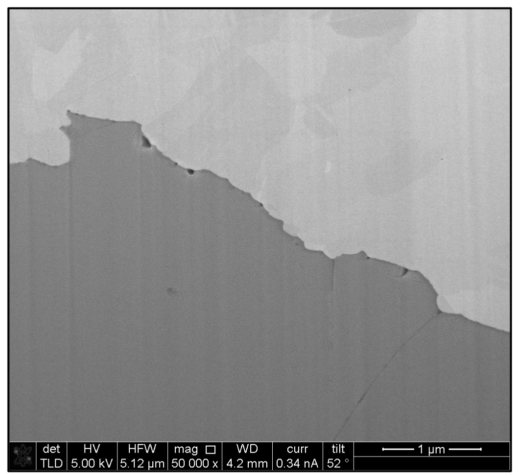
P type



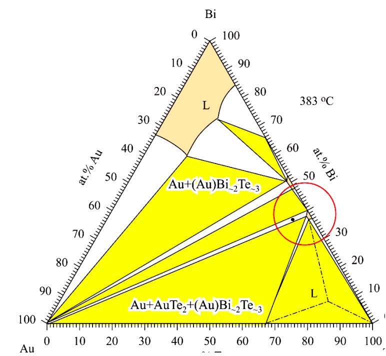


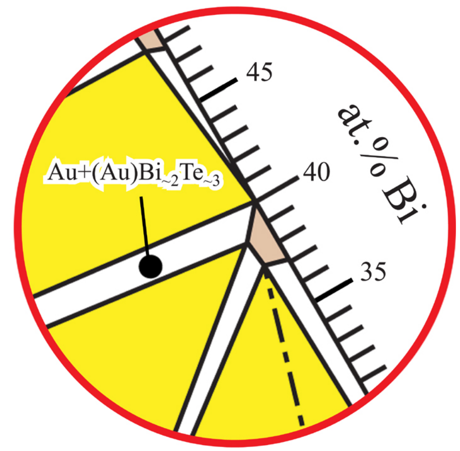
N-type





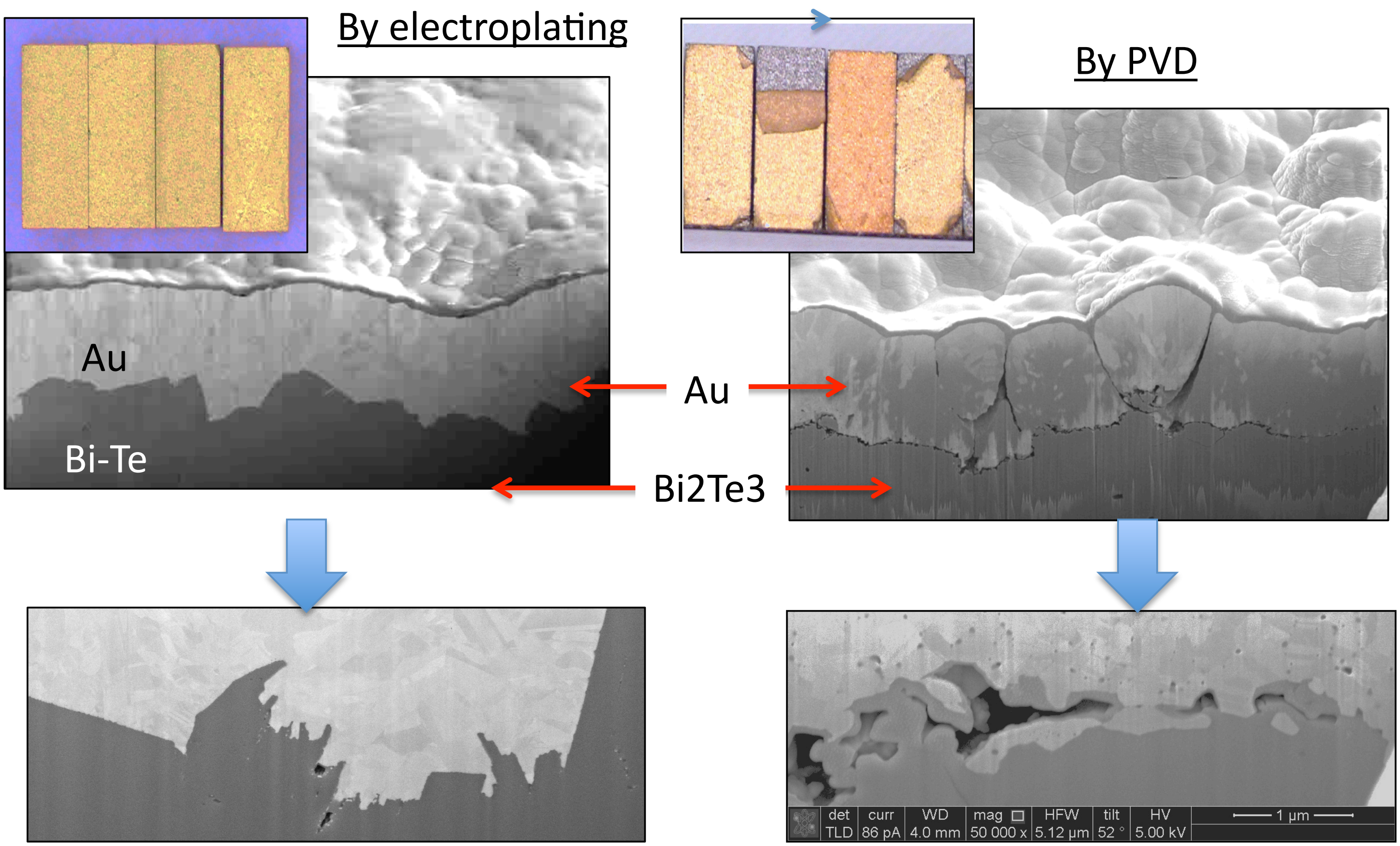
<u>Phase diagram shows low solubility of Au in Bi2Te3</u>





Root cause of interface voids?

Adhesion and structure integrity of Au metallization is process-dependent



3-D SEM image reconstruction using focus ion beam (FIB) shows thru-thickness pinholes and film defects of PVD Au.

By process of elimination, the 15um electroplated Au is selected for strong adhesion and low film defect

Process development and optimization completed for thin film Au metallization

15 um Au by PVD

Au delamination

200 nm Au by PVD

15-20 um Au by electroplating

20 um Pd, Ni, Co by electroplating w/ or w/o Sn-Au-solder

Metallization in stability at 240°C for 6 months

Incompleteed Au coverage led to adverse environmental-induced Sb or Bi oxidation & phase transformation.

Stable metallization at 240°C for 6 months

Stable contact resistance at 240°C

The final selection

Metallization instability at 240°C for 6 months

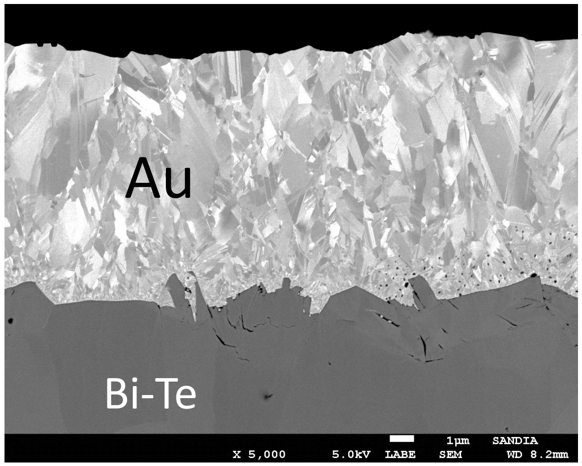
Reacted with Bi2Te3-based p- or n-type alloys

Go

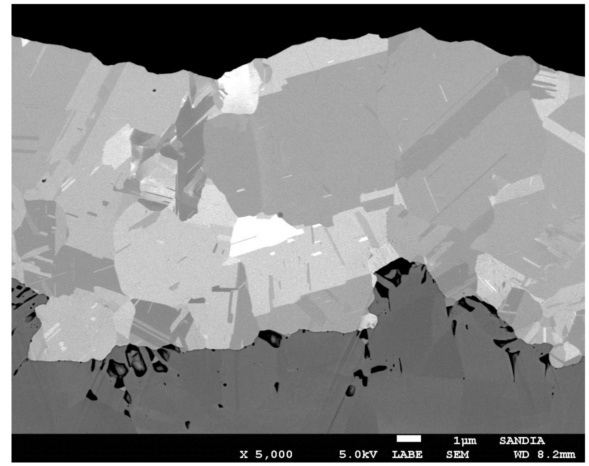
No-go

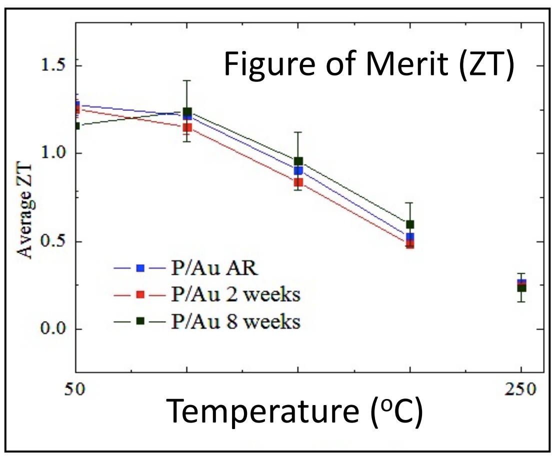
Grain growth/recrystallization has little effect on TE transport or contact resistance, therefore, not important to TE performance

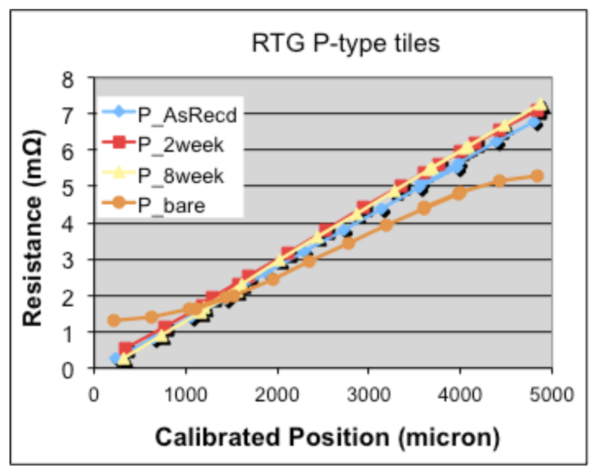
As-received



240°C/8



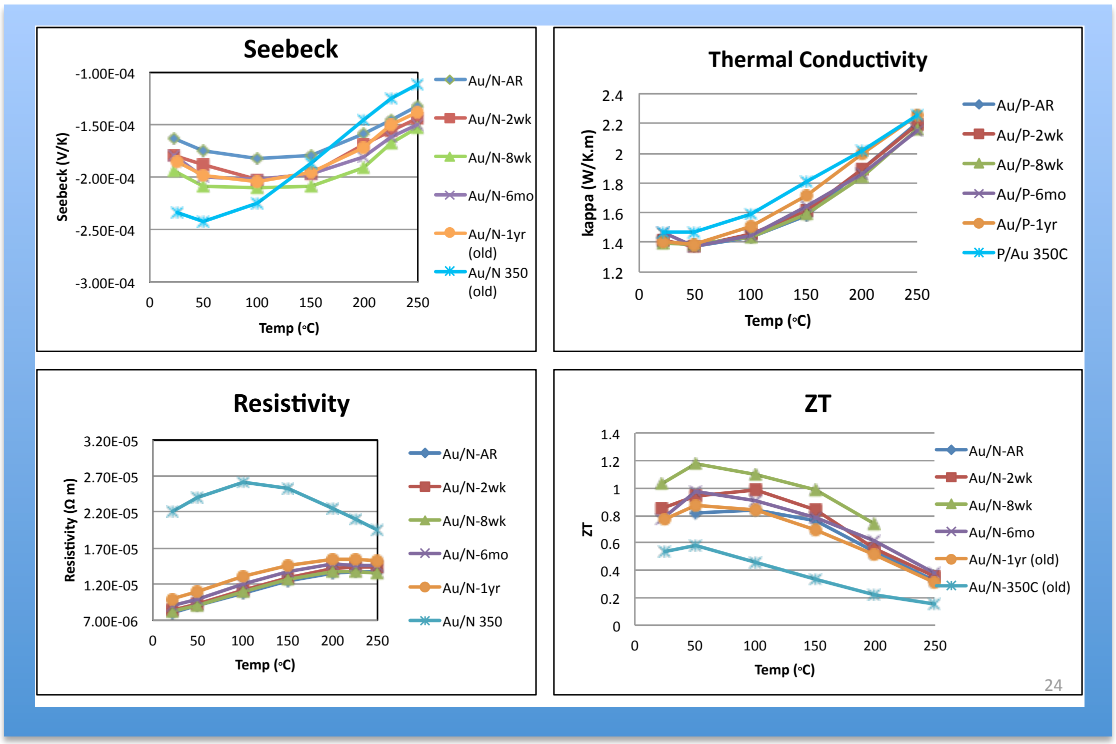




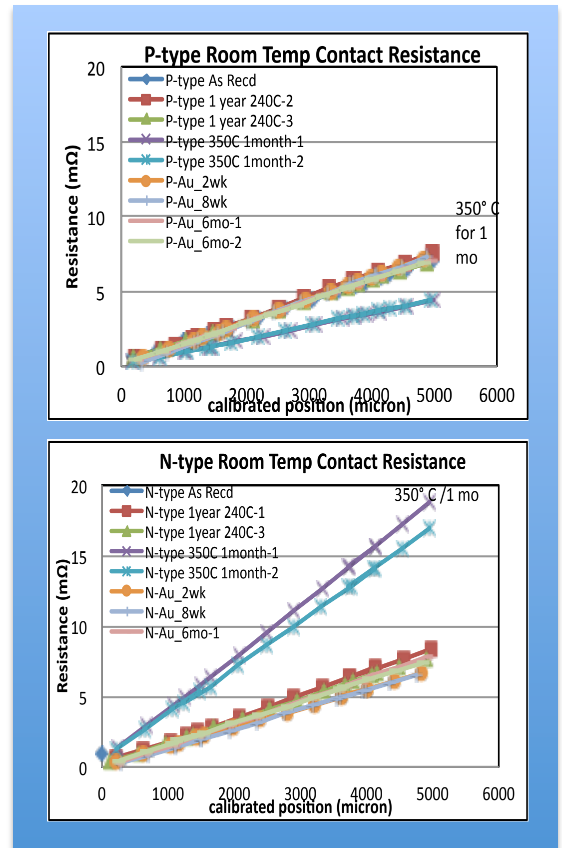
Pores at the interface are more visible in the annealed tiles that potentially could weaken the bond strength or structure integrity

TE transport property & contact resistance become unstable at ≤350°C

TE transport properties of n-type



Contact resistance

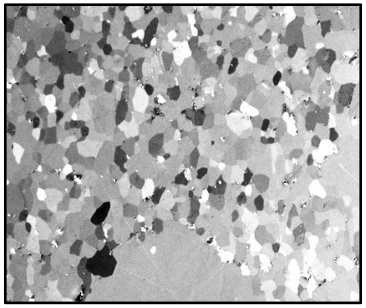


TE transport properties changes drastically, electrical resistivity in particular, at the accelerated aging at 350°C for a month.

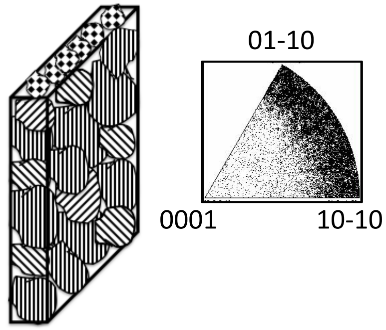
Materials science factors must be integrated into system engineering

p-n base alloy & polymer filler

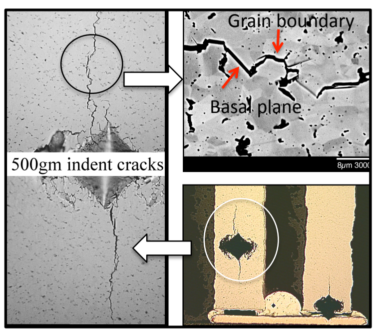
Microstructure



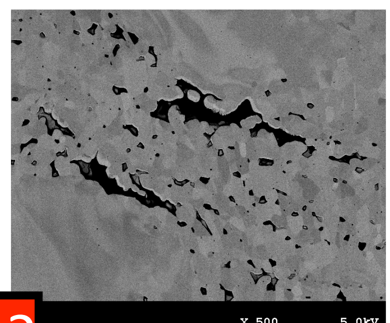
Anisotropy



Microstructure induced failure

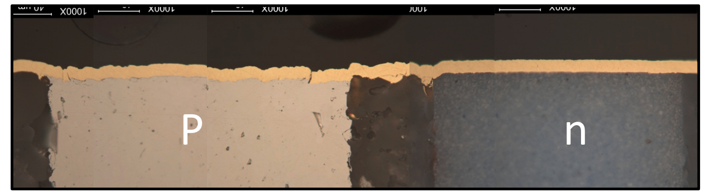


Process-induced defect

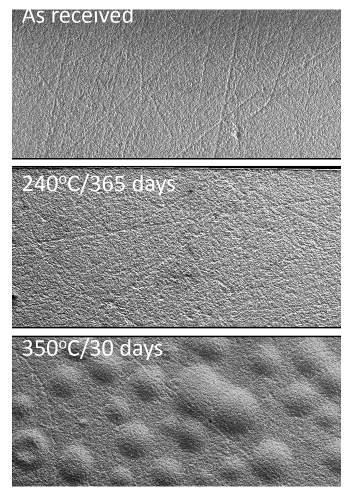


Thin film metallization

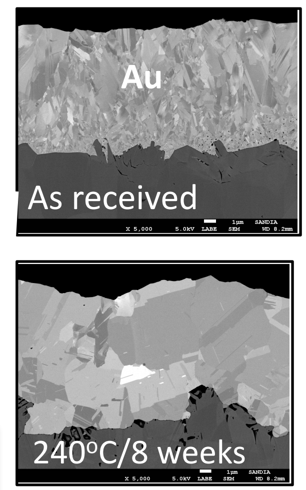
Device construction/material compatibility



Thin film adhesion & thermal stability



Temp.



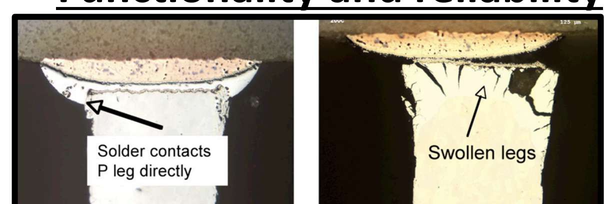
TE transport

$$ZT = \frac{S^2}{\rho\kappa} T$$

Power generation efficiency

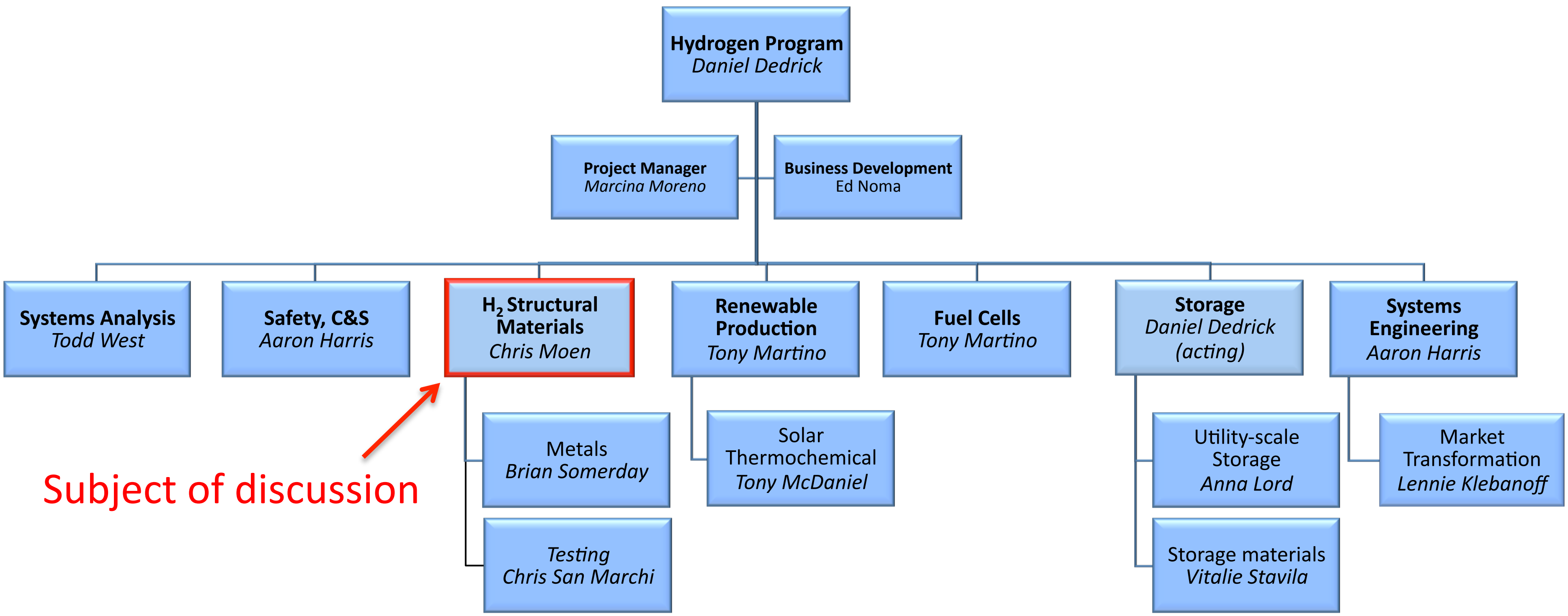
$$\eta = \frac{T_h - T_c}{T_h} \frac{\sqrt{1 + ZT_{avg}} - 1}{\sqrt{1 + ZT_{avg}} + T_c / T_h}$$

Functionality and reliability

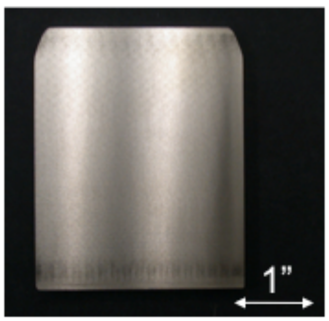


Programmatic infrastructure for H2 Program at Sandia

- *Enhancing our critical H2 science and technology capabilities*
  - *Partnerships with industry, labs, and through our Livermore Valley Open Campus REACH Initiative.*

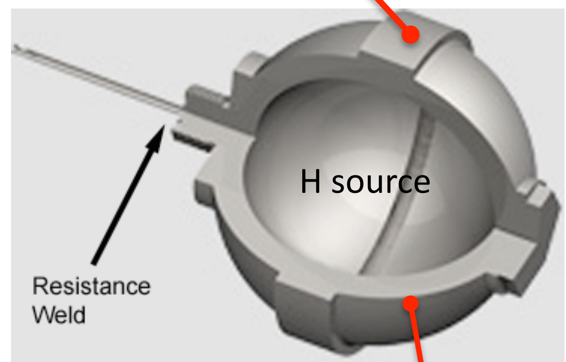


S&T for tritium/hydrogen reservoir is SNL's core competency for the defense & energy security missions



Metal Forming thru casting /forging...

Metal joining/welding



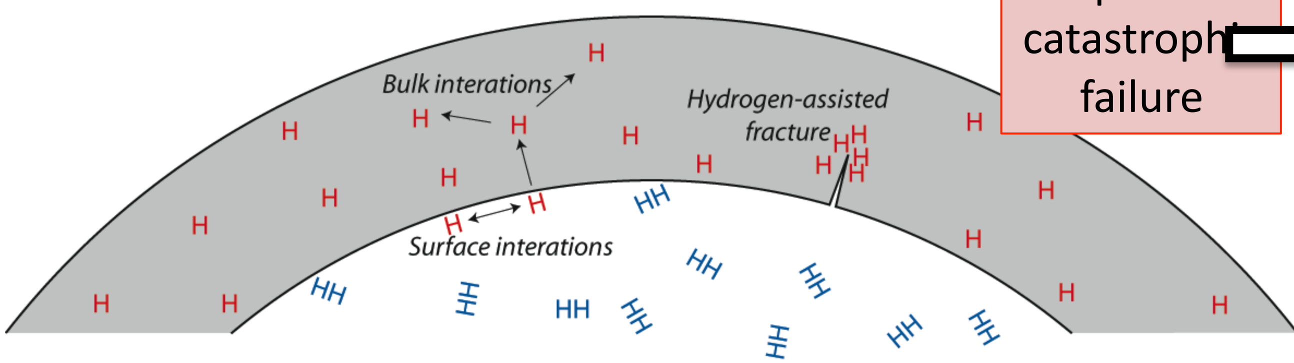
A reservoir design based on sound science

<u>Material science factors:</u>

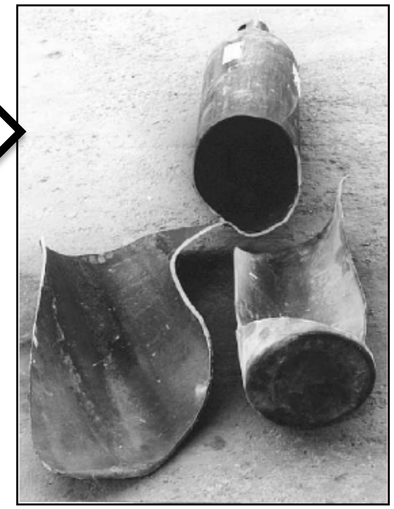
- *Process-induced physical and chemical metallurgy:*
  - Mechanical properties, microstructure and chemical uniformity?
  - Processing – structure - performance relationship?
- *Environmental effect from H-isotope exposure?*

Tr/Hydrogen science is critical for engineering H-storage reservoirs

1) *Hydrogen-surface interactions:* molecular adsorption and dissociation producing atomic hydrogen chemisorbed on the metal surface
2) *Bulk metal-hydrogen interactions:* dissolution of atomic hydrogen into the bulk and segregation to defects in the metal (i.e., transport and trapping)
3) *Hydrogen-assisted cracking:* interaction of hydrogen with defects changes local properties of the metal leading to embrittlement and possibly failure



To prevent catastrophic failure

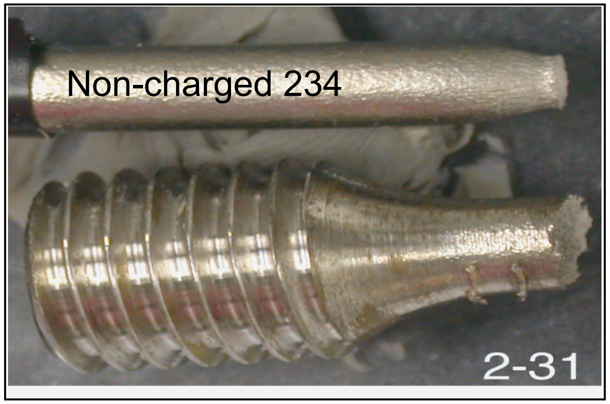


Science-based understanding of embrittlement essential for ensuring safety and reliability of hydrogen technology

Brittle fracture is observed in the H-precharged stainless steel specimens

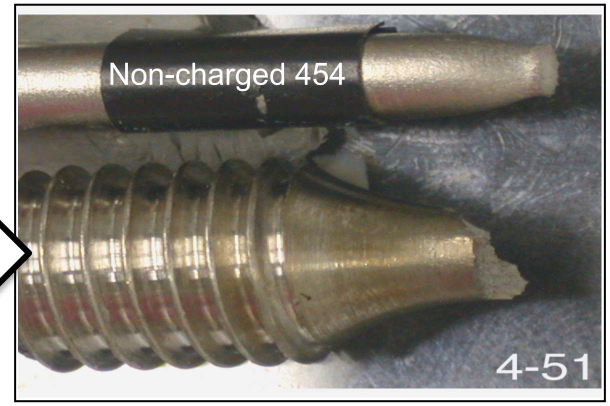
Tensile tested specimens

Alloy II



Brittle fracture

Alloy VI



alloy	ASTM grain size	Tensile testing at 293 K			Tensile testing at 223 K		
		Yield strength (MPa)	Reduction of area (%)		Yield strength (MPa)	Reduction of area (%)	
			Non-charged	Hydrogen-precharged		Non-charged	Hydrogen-precharged
II	6	214	82	57	288	78	21
IV	4	221	73	40	312	75	20

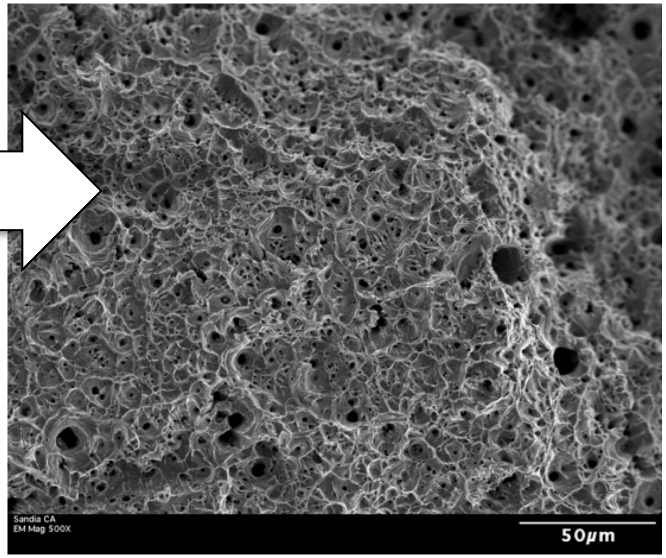
Scientific rationale behind the embrittlement?

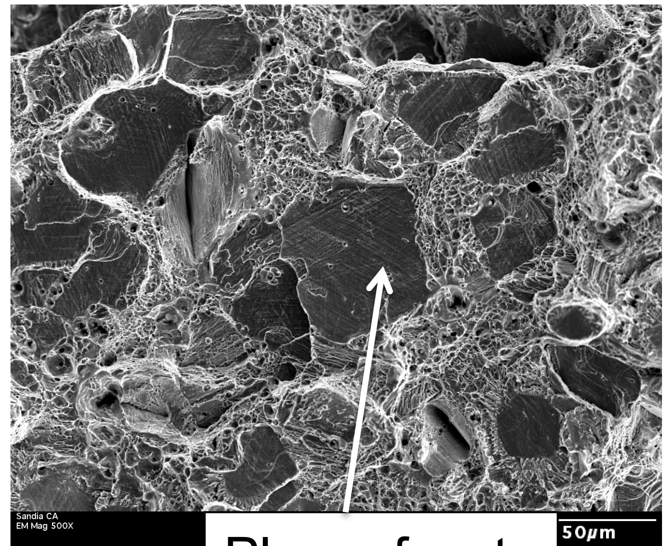
Faceted brittle fracture observed in H-precharged fracture surface

Non-charged ductile fracture

H-precharged brittle fracture

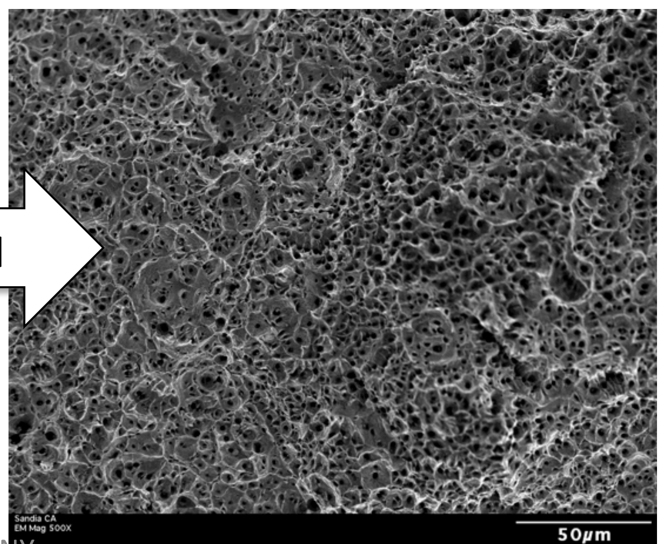
Alloy II

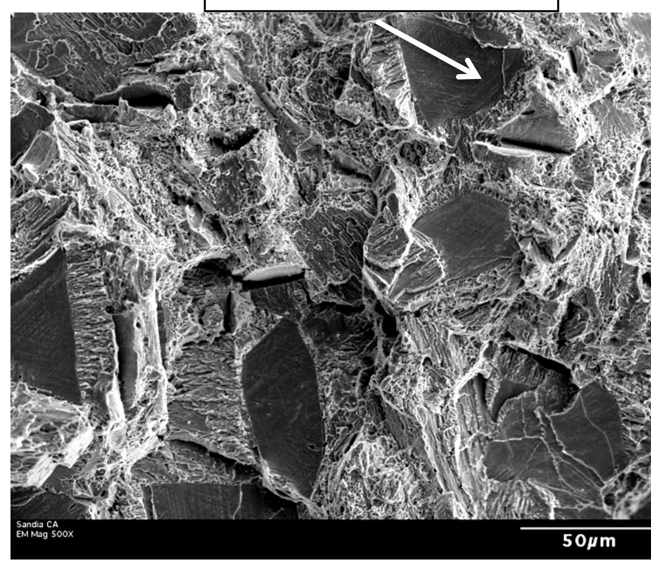




Planar facets

Alloy VI

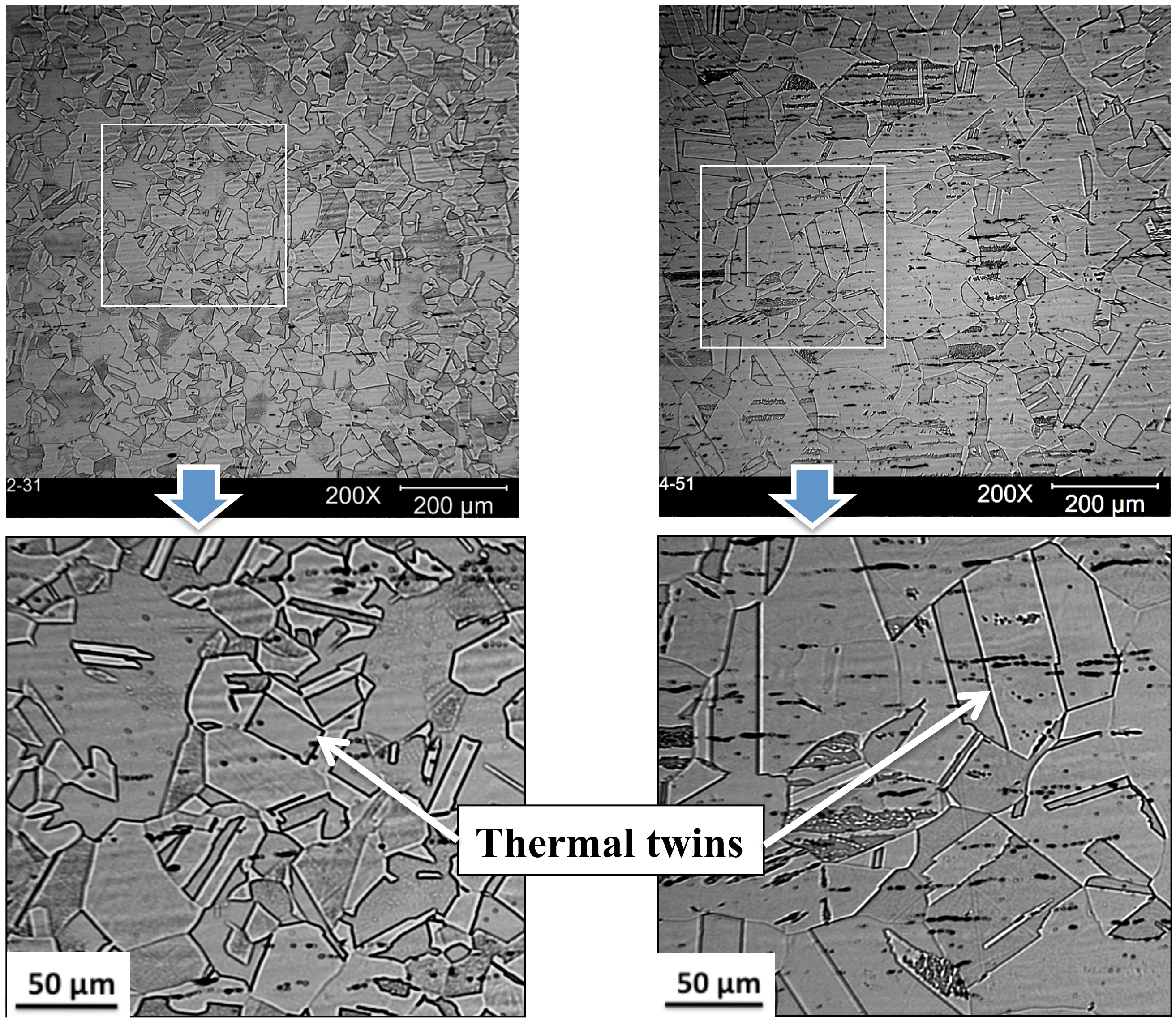




Thermal twins are commonly seen in both stainless steels: Alloy II (#231) and Alloy VI (#451)

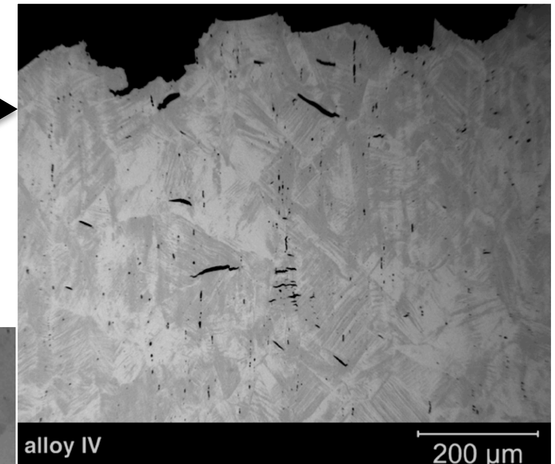
Fine grained alloy II

Coarse-grained alloy VI

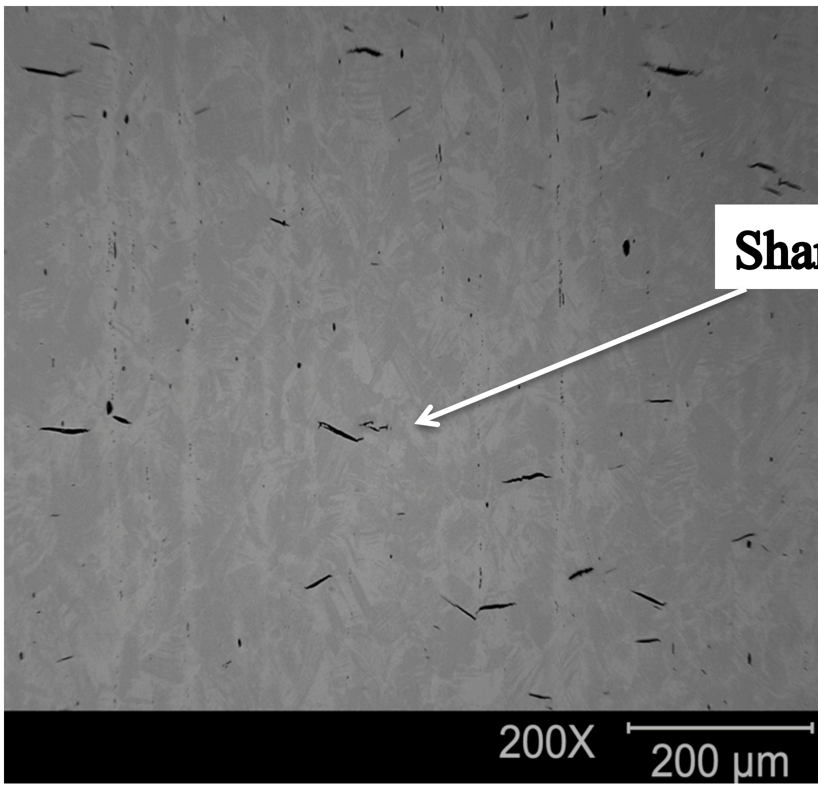


Sharp cracks seen in the tensile-tested specimen located at the planar boundaries of certain microstructure features

Cracks seen on the cross section near fractured face

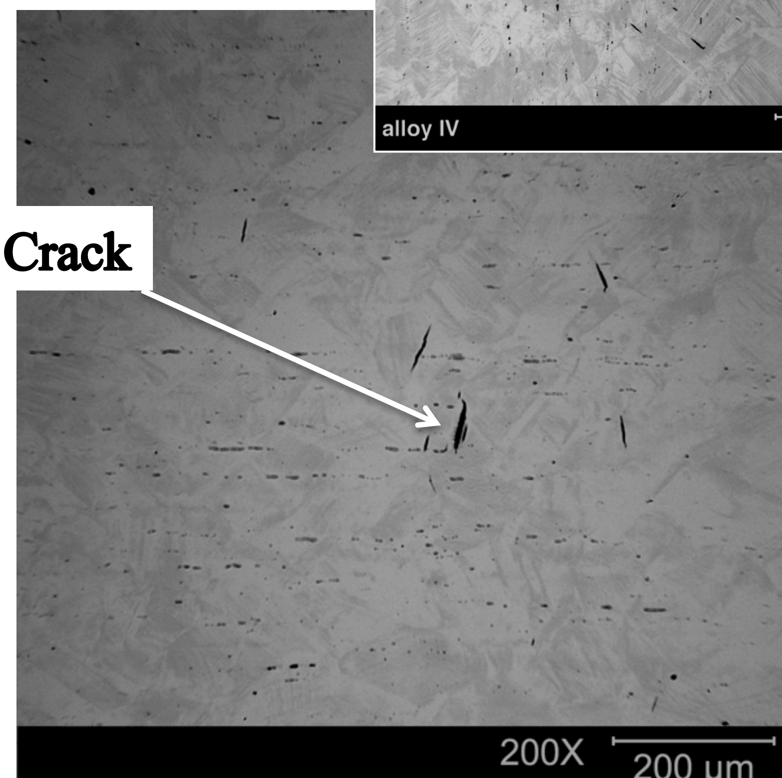


Alloy II



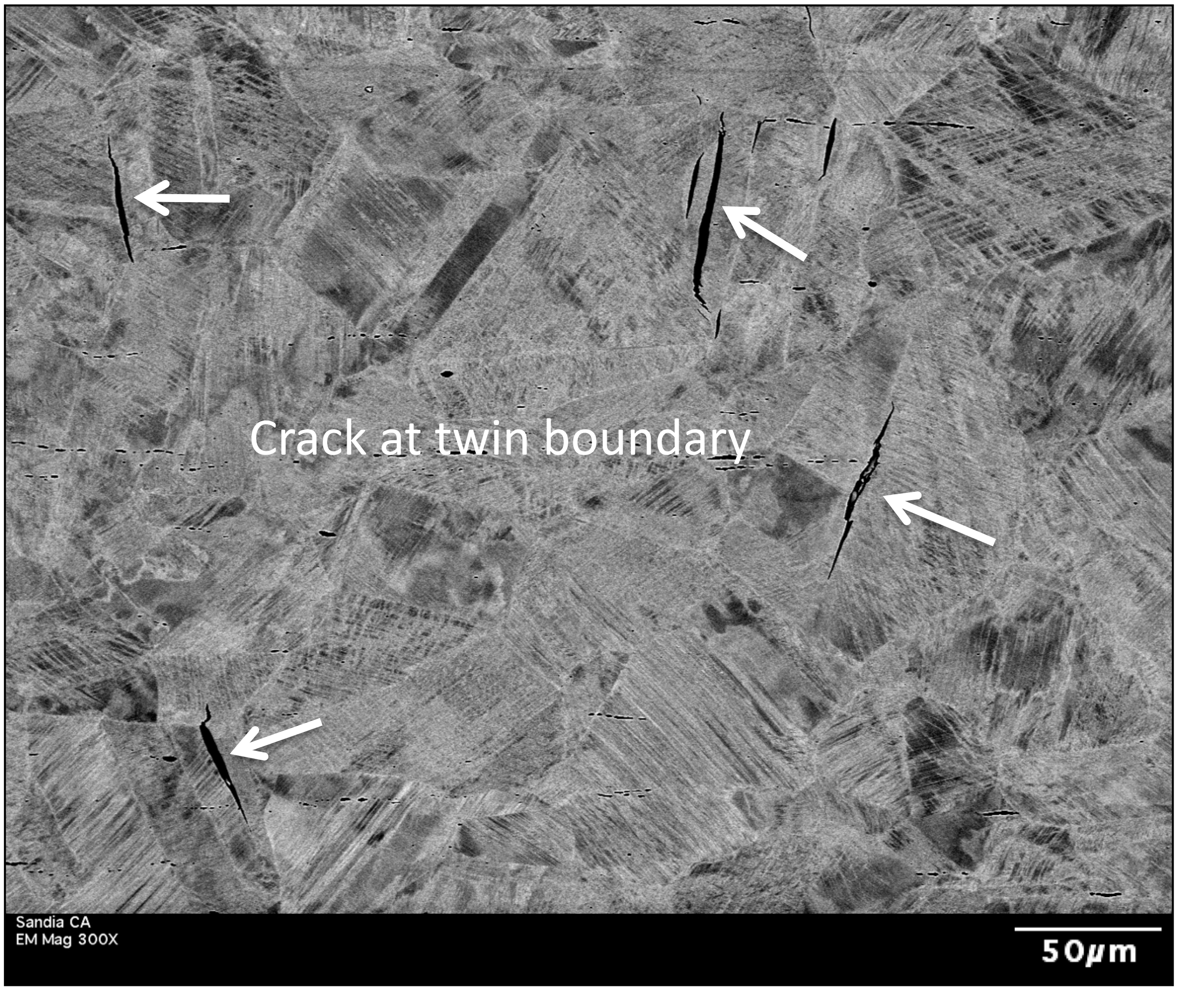
Sharp Crack

Alloy VI



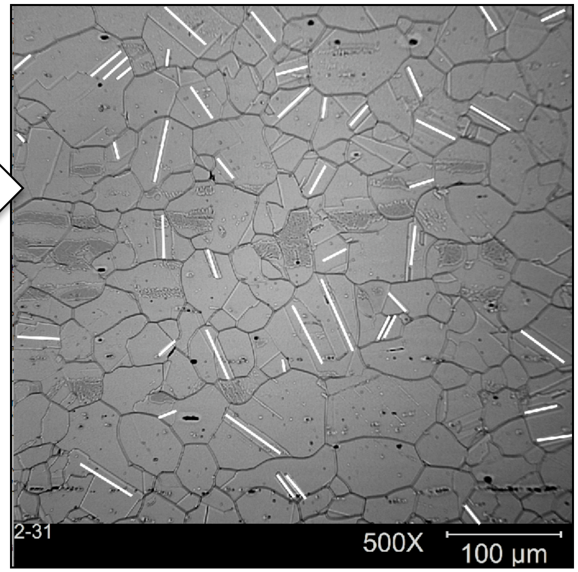
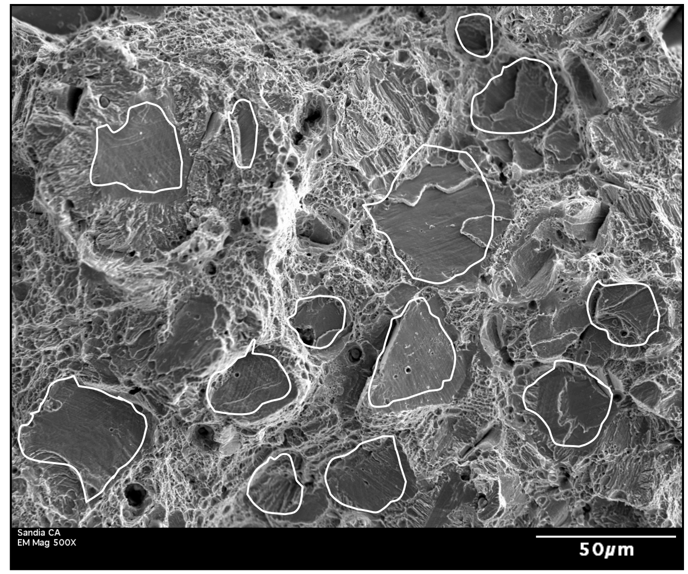
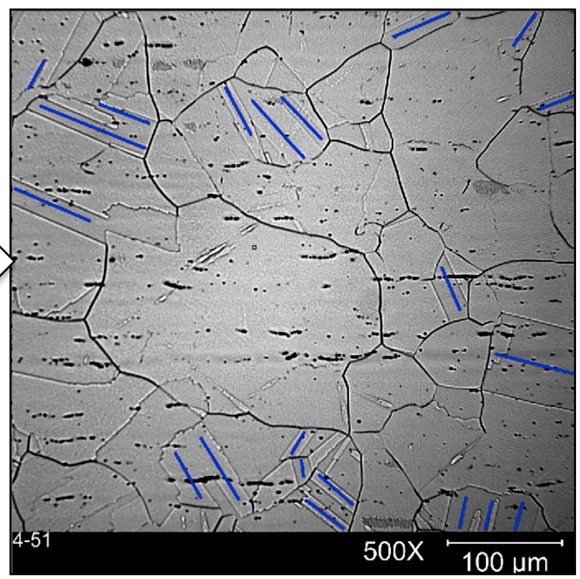
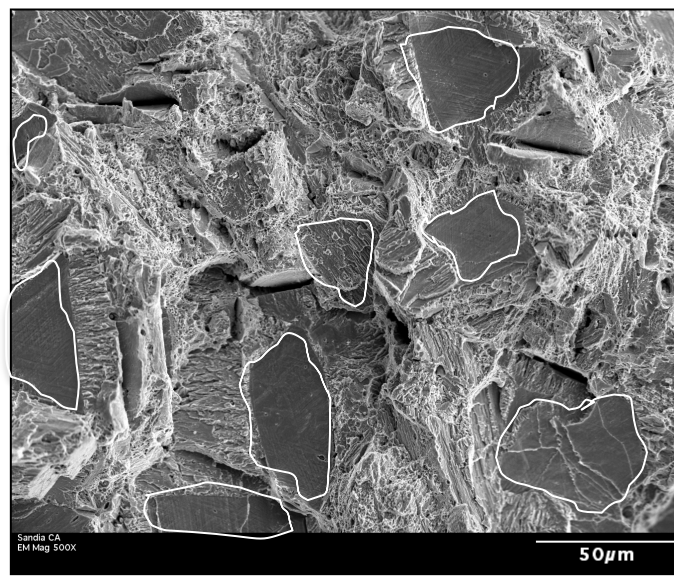
SEM image shows the sharp cracks situated mostly at the planar boundaries of thermal twins

Cross section near the fracture surface



Population & size of the planar fracture feature match the size and density of thermal twins on the cross section

National Nuclear Security Administration

	Optical image of the cross section	SEM image of the fracture face
Alloy II		
Alloy VI		

Comparable twin population per unit area estimated between the cross section and fracture face

Alloy II	Grip section	Gauge section
Optical/SEM image magnification	# of twins	# of facets
100x	194	178
200x	103	78
300x	52	53
500x	42	37

Alloy VI	Grip section	Gauge section
Optical/SEM Image magnification	# of twins	# of facets
100x	113	120
200x	56	61
300x	28	32
500x	21	24

For a good statistic, the population of thermal twin is counted from both optical and SEM images at several magnifications..

Mitigation strategy and/or engineering solution for hydrogen embrittlement?

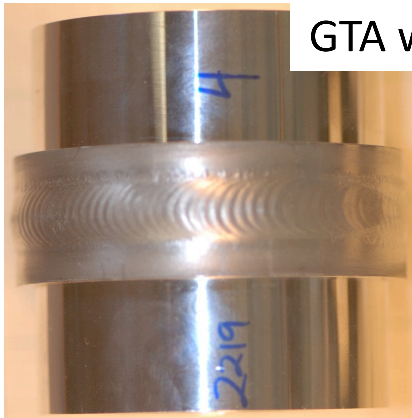
- Control adverse metallurgical feature(s) thru alloy/microstructure engineering, during alloy forming or post forming heat treatment.

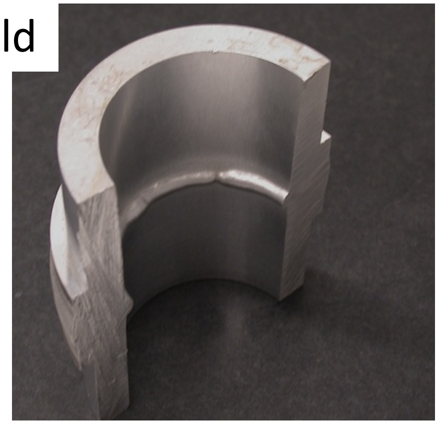
or

- Alternative alloy selection, such as high strength aluminum alloy which is know to be less susceptible to hydrogen embrittlement

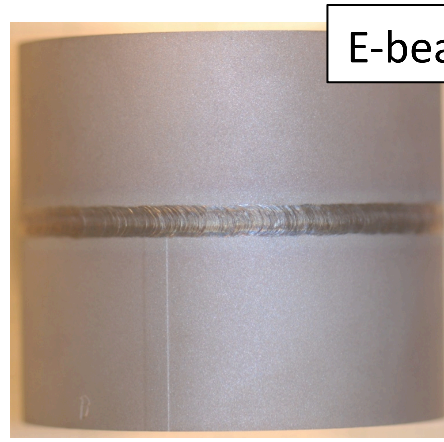
Great success in developing alternative to stainless steel, e.g. 2219 aluminum alloy and its welding process.

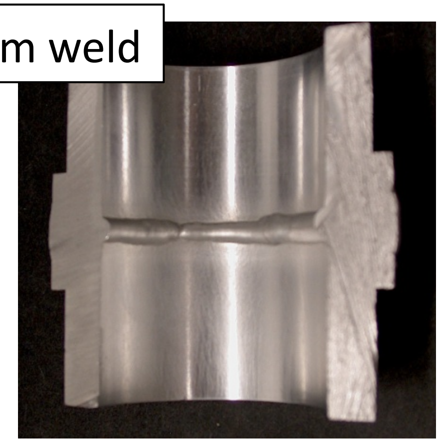
GTA weld



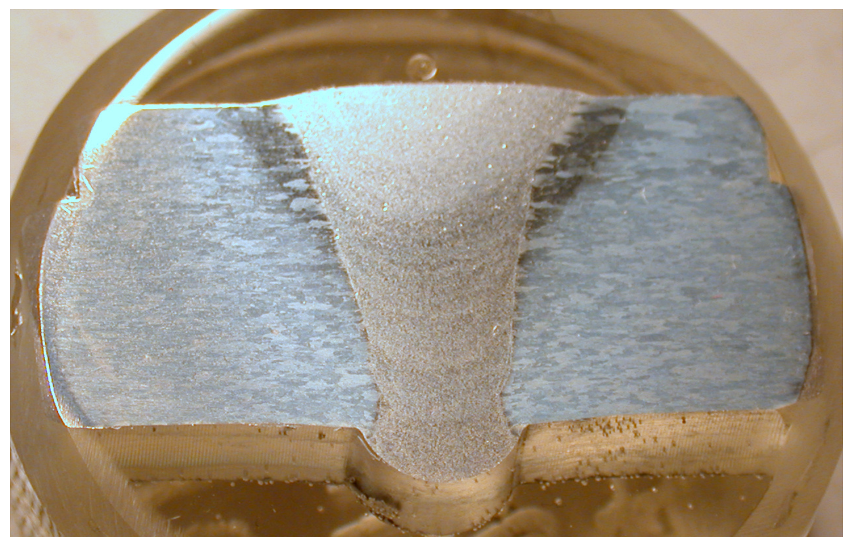


E-beam weld



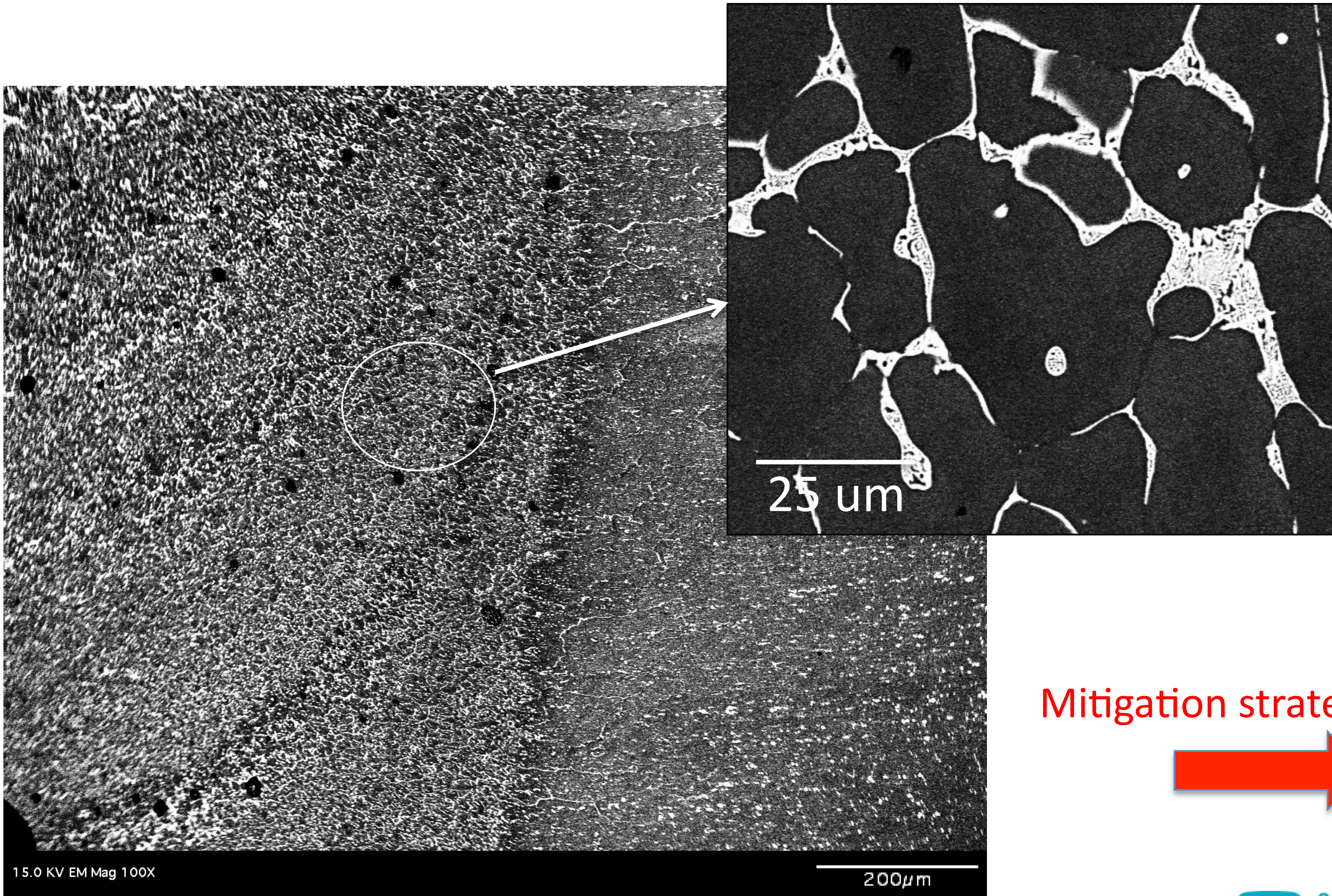


Typical polished cross section of Al GTA weld



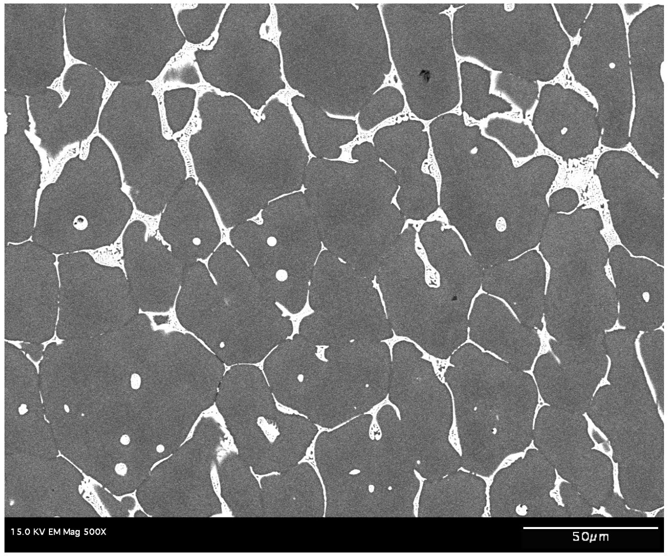
Al-welding is one of the technical challenge to be overcome.

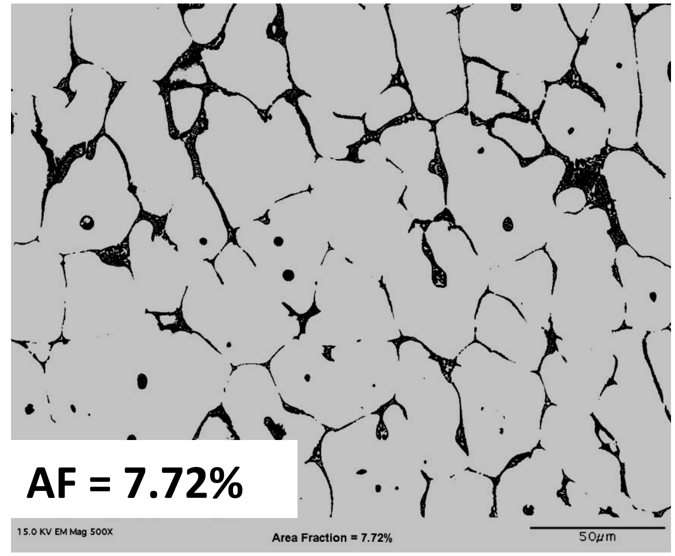
2nd phase formation & strength variation near the Al-weld interface is vulnerable to a premature cracking.

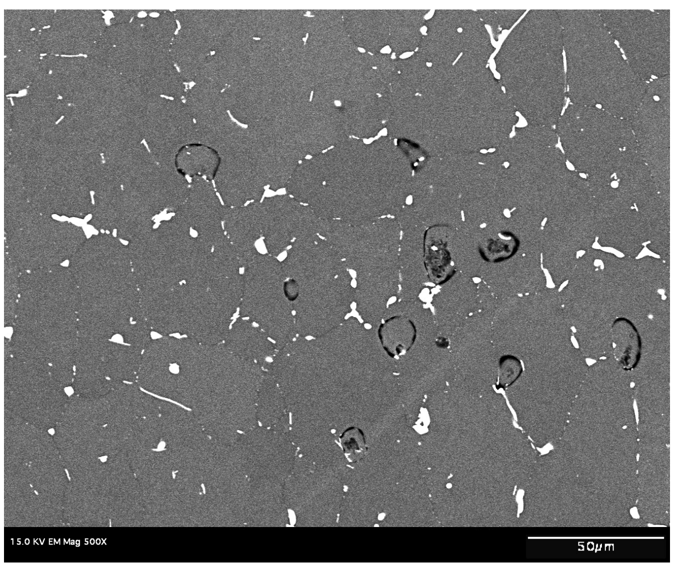


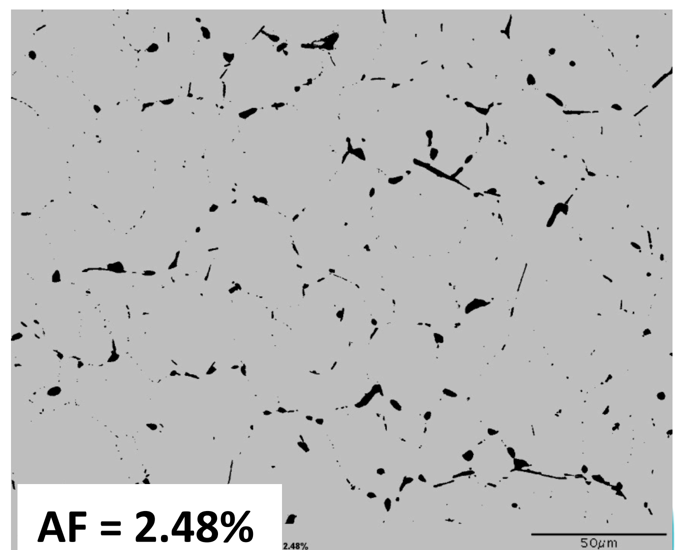
Mitigation strategy?

Lowering the 2nd phase volume fraction is achieved thru post-weld annealing









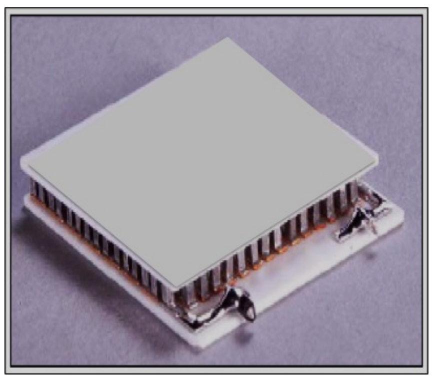
Technical accomplishments in energy system engineering

Develop materials and Capabilities

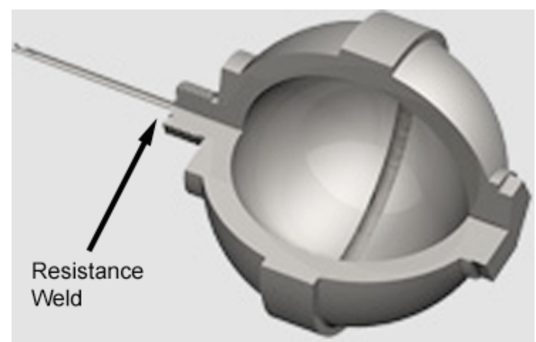
Enabling design and build

Reliable High performance energy systems for defense or commercial use

Thermoelectric module



H2-reservior structure



Successful in developing a TE module that meets the power requirement

A good success in developing a Al-reservoir for H-embrittlement mitigation

Integrate basic science, engineering science and system engineering is our strategy for achieving engineering objectives

Basic science and mechanisms

Provide scientific rationale and guidance for:

Engineering science to support component design & construction

- Alloy engineering & process optimization
- Predictive model development for validating system reliability and performance

System design/construction & engineering

Ensure the ultimate engineering system is design/build based on sound science