NSF-DOE TE Partnership: Integrated Design and Manufacturing of Cost-Effective & Industrial-Scalable TEG for Vehicle Applications

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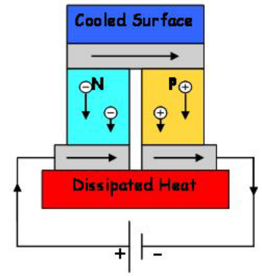
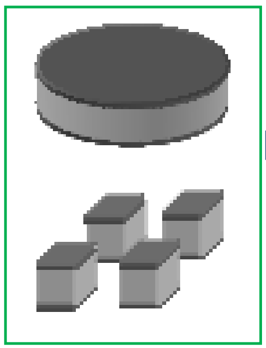
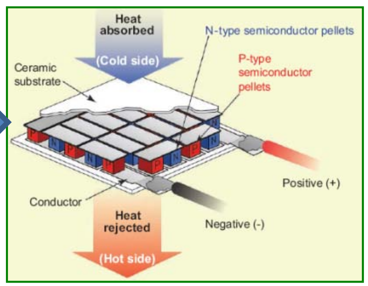
2011 DOE Thermoelectrics Workshop, Jan 3-6th, San Diego, CA

Thermoelectric Waste Heat Recovery

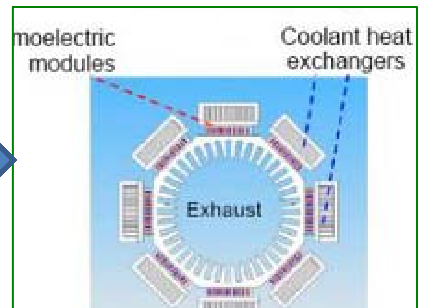
- **Traditional TEGs**
  - Material synthesis →
  - Module assembly →
  - Subsystem integration →
  - Vehicle Integration



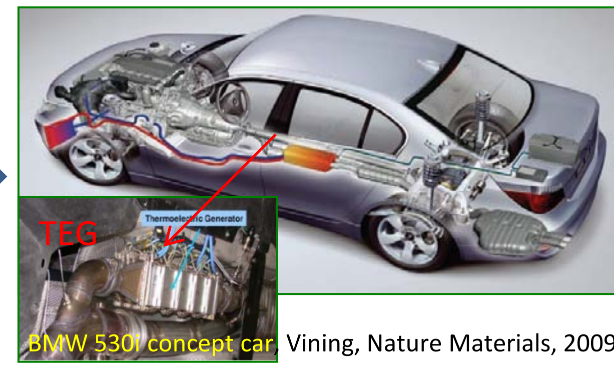




J. Bell, Science, 2008



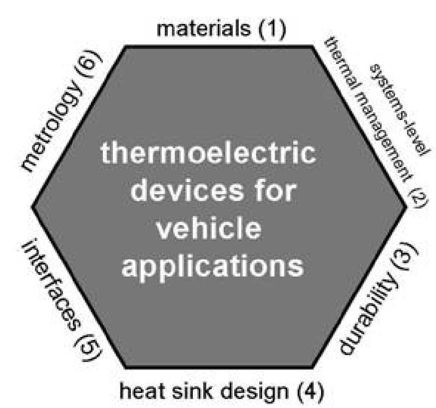
J. Fairbanks, DOE, 2008



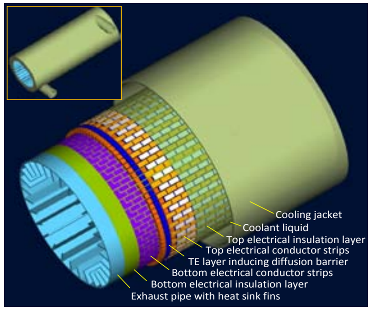
Vining, Nature Materials, 2009

Challenges

- Multiple-step assembling
- Interface and durability (soldering, clamping)
- Considerable vehicle modification
- Materials (cost, toxicity, synthesis time)



→ Integrated Design and Manufacturing



System-Level Approach

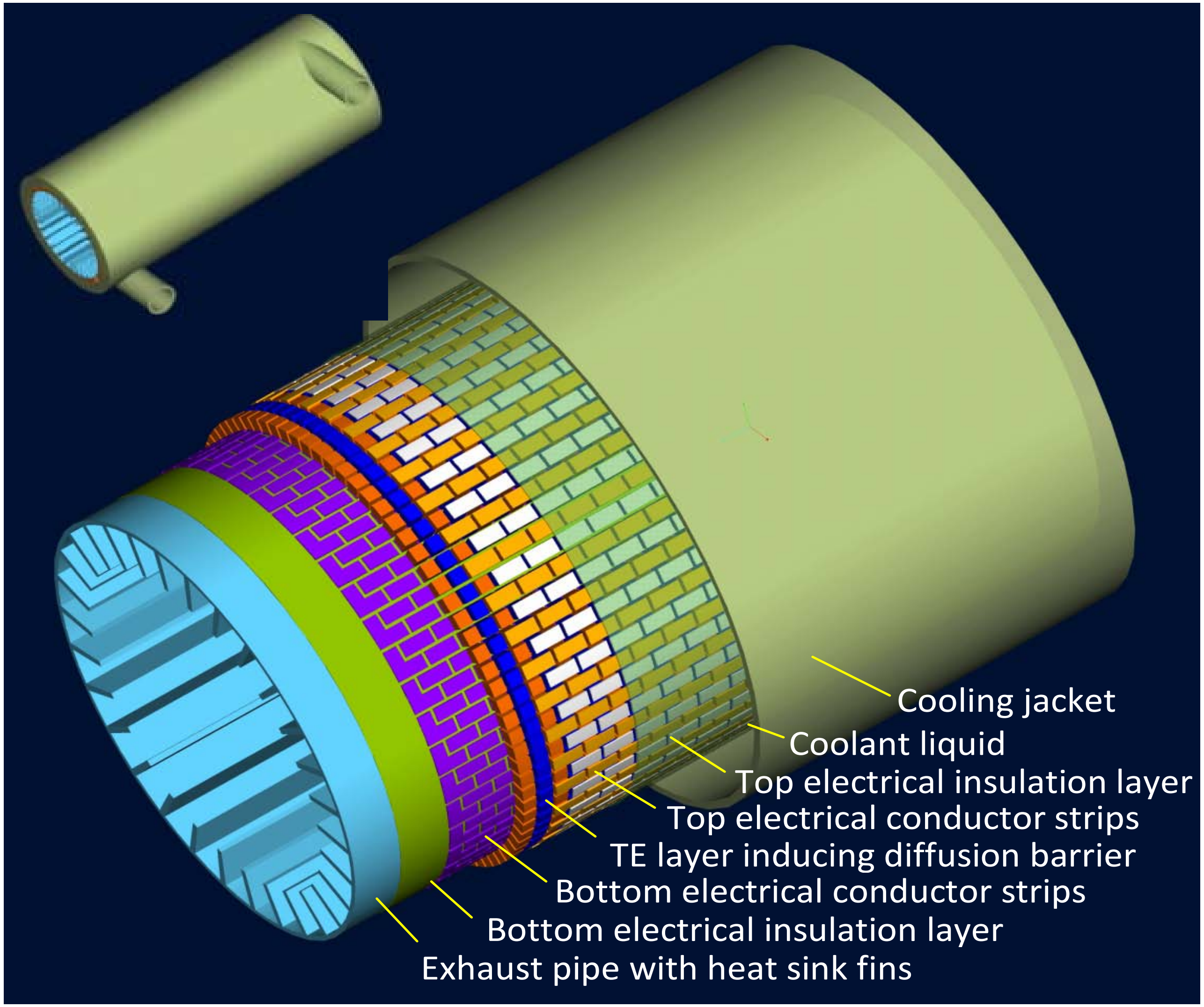
Design
- Mechanical and Thermal
- Manufacturing

Materials
- Metal Silicides
- Skutterudites

Process
- Nonequilibrium Synthesis
- Thermal Spray

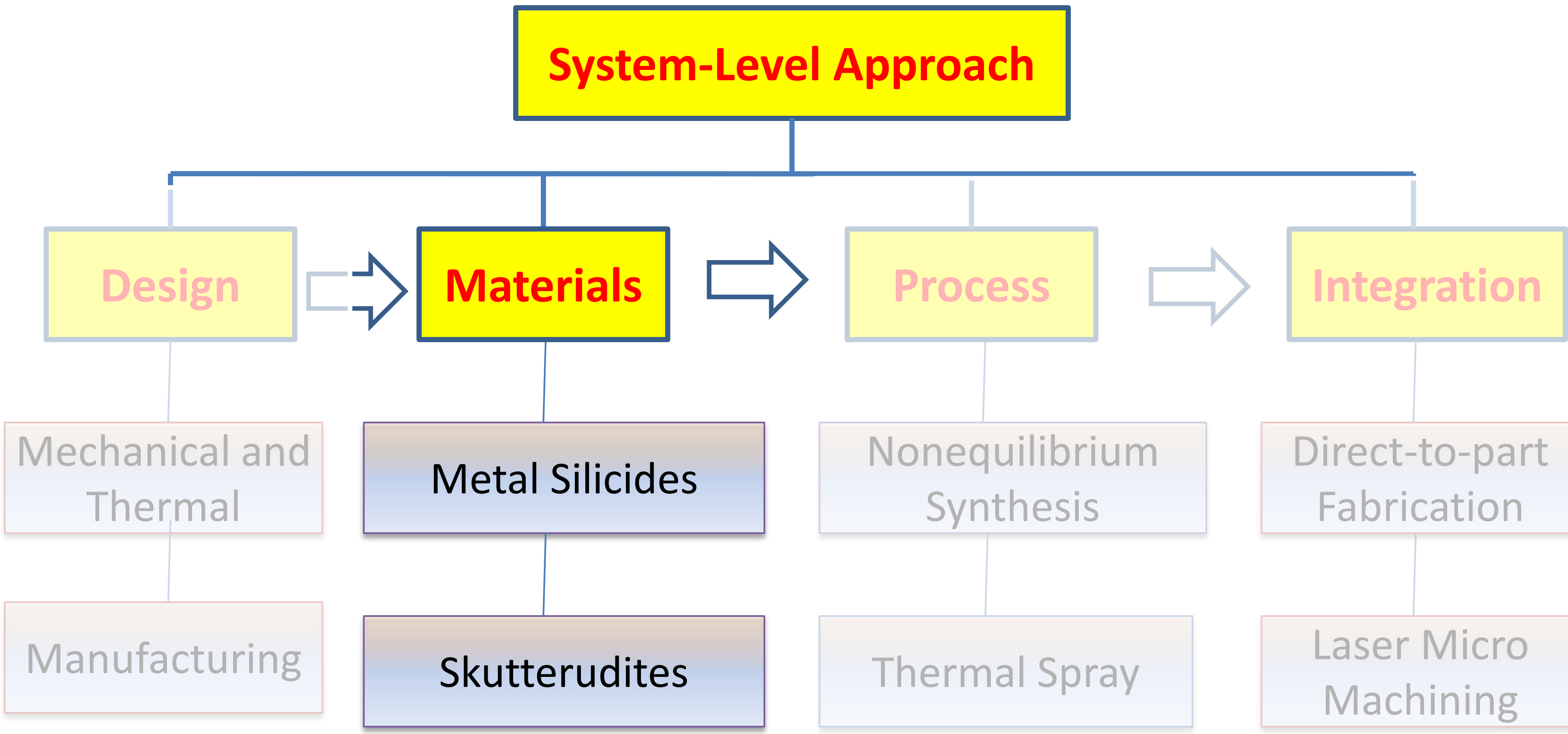
Integration
- Direct-to-part Fabrication
- Laser Micro Machining

Integrated Design and Manufacturing



- Abundant low-cost feedstock
- Direct fabricate on exhaust pipes
- Non-equilibrium synthesis for improved ZT
- Industrial progress: thermal spray and laser micromachining
- Reliable interface and durability without soldering or clamping

→ Integrated Design and Manufacturing

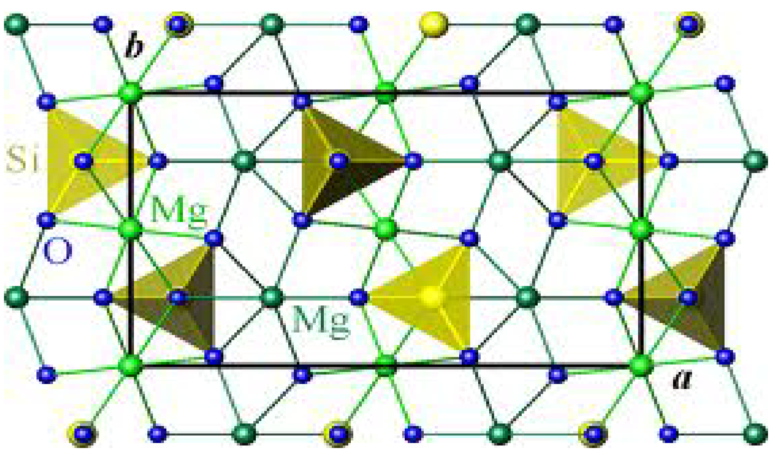


Metal Silicide (Mg_2Si)

- Metal Silicides: slightly lower *ZT*,
  <u>but</u> abundant, inexpensive, no toxicity.
- ***ZT* ~ 1.1** near 800K ($Mg_2Si_{1-x}Sn_x$),
  Bi/Al doped

Comparison : Abundance, Material Cost
Environmentally Hazardous Substance

	Mg_2Si						
	Mg	Si	Bi	Te	Pb	Co	Sb
Reserves (ppm)	32,000	267,700	0.06	~5 (ppb)	8	29	0.2
Cost (K¥/MT)	200	90	849	9000	98	3500000	430
Toxicity	NO	NO	YES	YES	YES	YES	YES



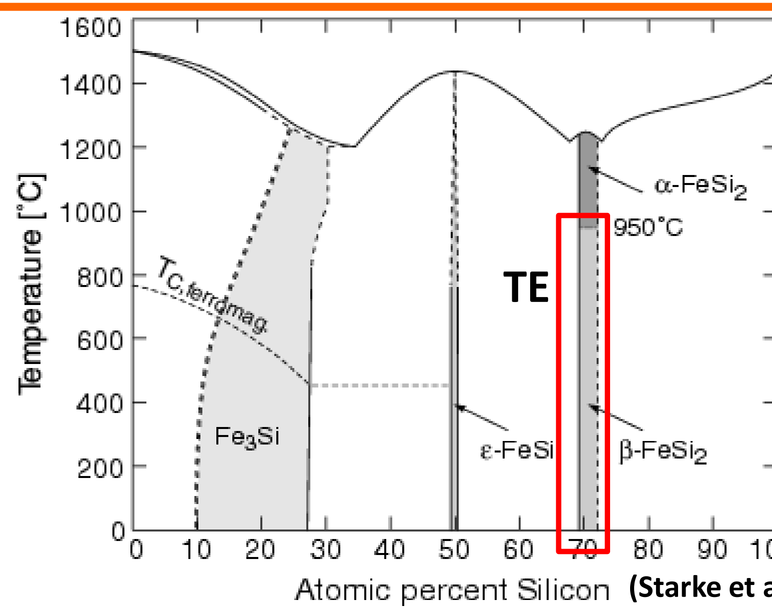
Source: Tokyo University of Science

R. Szczech and Song Jin 2008 and references therein

V. K. Zaitsev et al, 2006, Physical Review B

Metal Silicide ($FeSi_2$)

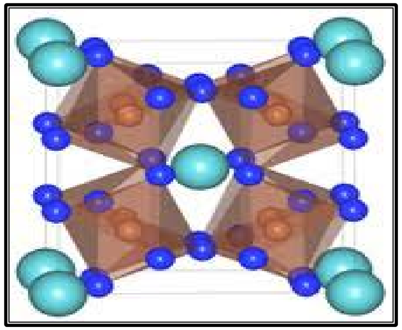
- β-$FeSi_2$ has TE properties. N-type doping with Co, p type with Mn or Al
- *ZT* ~ 0.06-0.15 at 400 – 600 °C
- Process Study: Thermal Spray used to synthesize bulk β-FeSi2
- *ZT* can be higher than by hot pressing !



(Starke et al 2001)

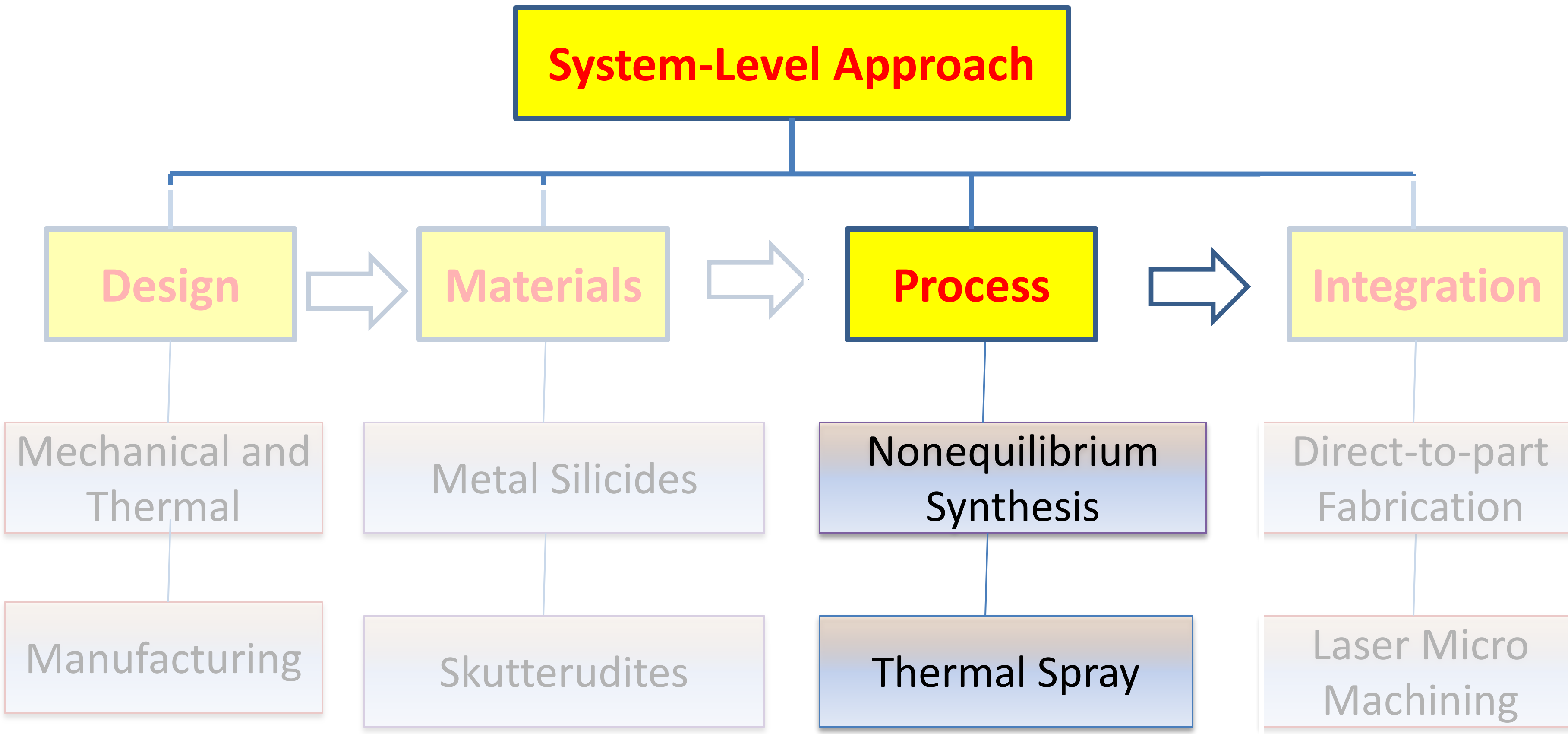
Filled Skutterudites

- Fill the void with low-coordination ion: phonon scattering to reduce thermal conductivity
- ZT = 1.4 reported



Co-PI Qiang Li at BNL2009

→ Integrated Design and Manufacturing

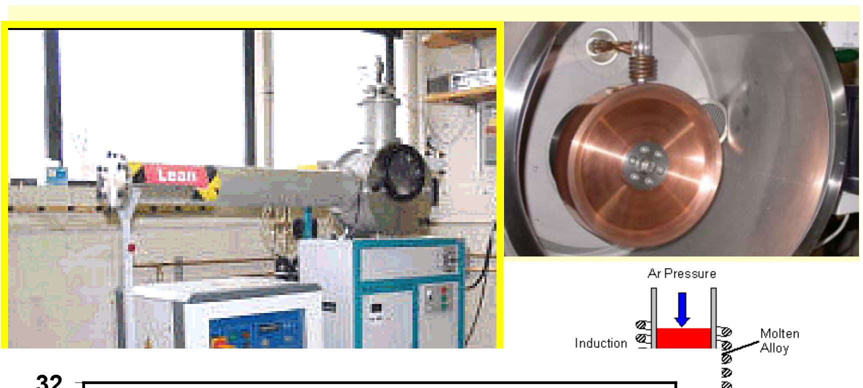


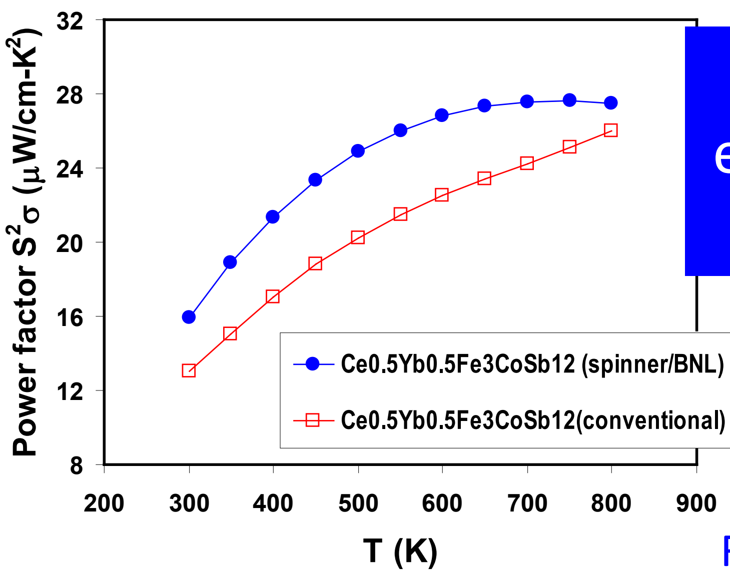
Non-Equilibrium Synthesis Method

Rapid solidification starting materials into near amorphous ribbons **in seconds**

→

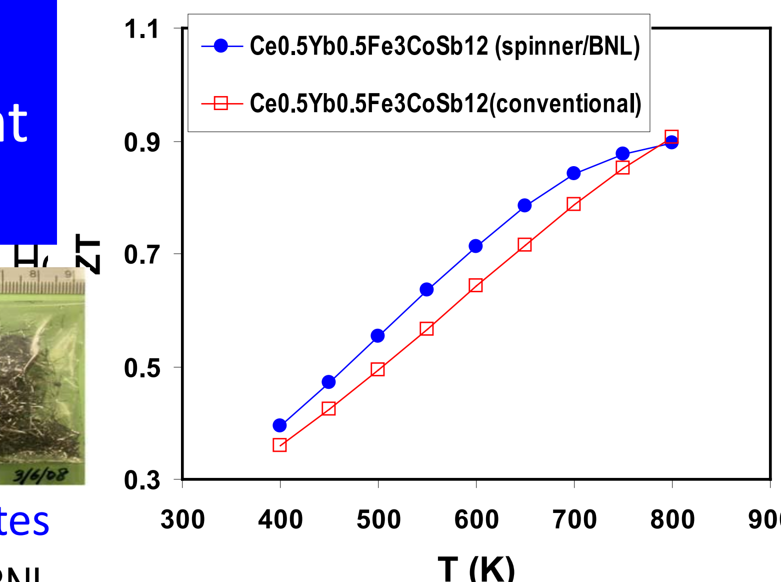
Direct conversion and densification under high pressure **in minutes**





20%-30% enhancement in Power

Filled Skutterudites



Dr. Q. Li (co-PI), Head of Advanced Energy Materials Group, BNL

Non-Equilibrium Synthesis Method

Conventional TE Synthesis

Melting

Quench into ingot

Powdering, sintering (days to weeks !)

High pressure densification

Advantage of Non-equilibrium Synthesis

- Reduced processing time from days to minutes
- Higher density and mechanical strength
- More control of micro- to nano-structure

Non-equilibrium Synthesis Techniques (e.g., Melt-Spinning)

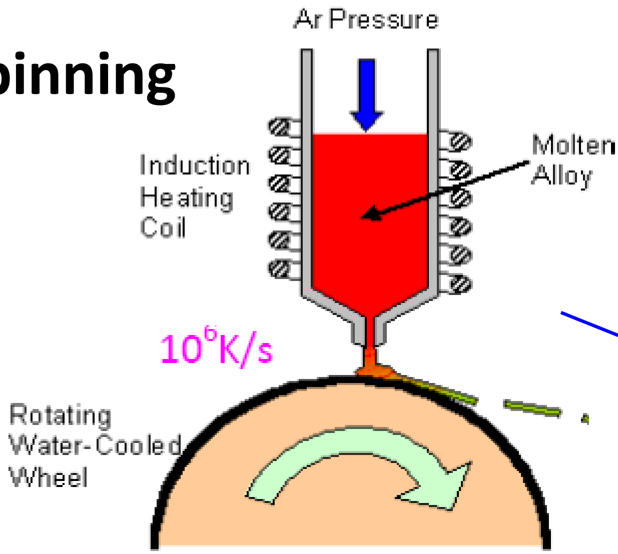
Rapid solidification into amorphous ribbons

(few seconds)

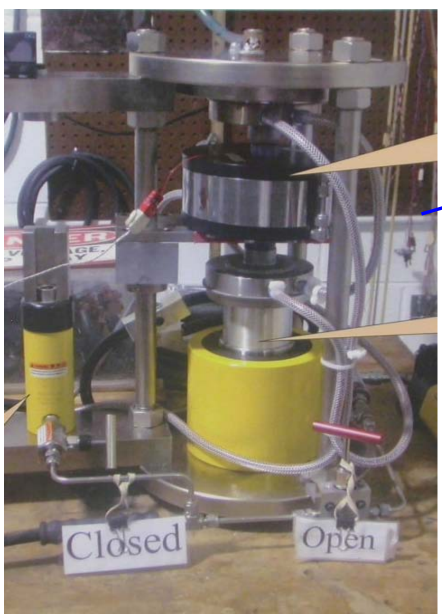
High pressure densification

Practical Non-Equilibrium Synthesis: Thermal Spray

Melt spinning



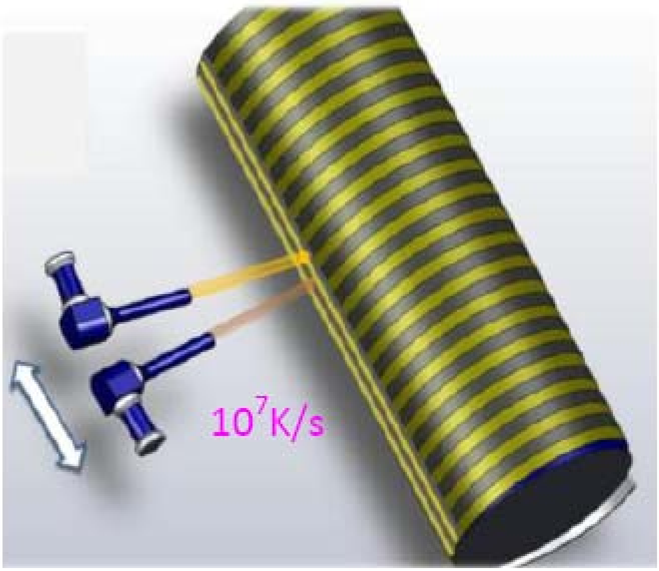
Hot press



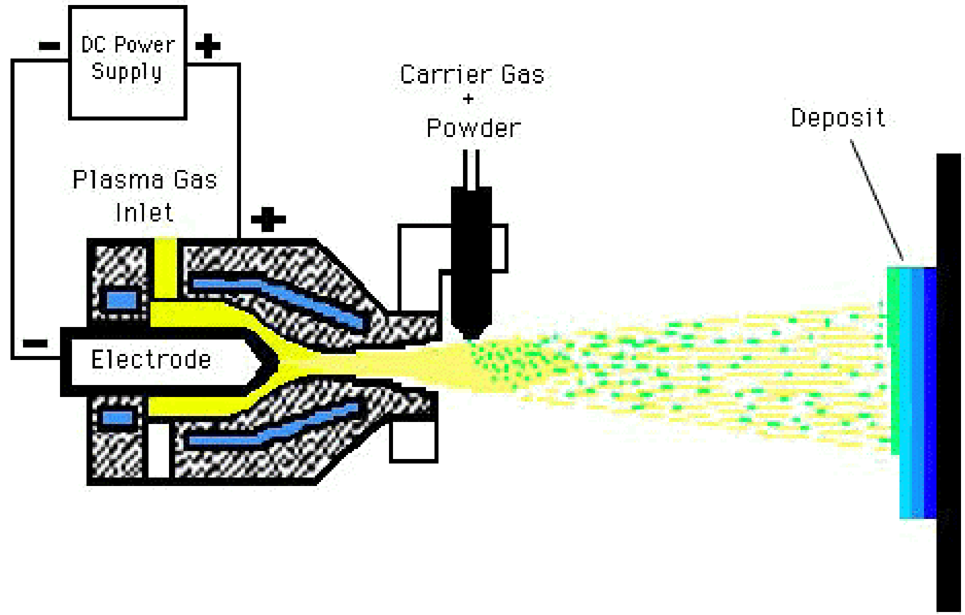
Rapid quench

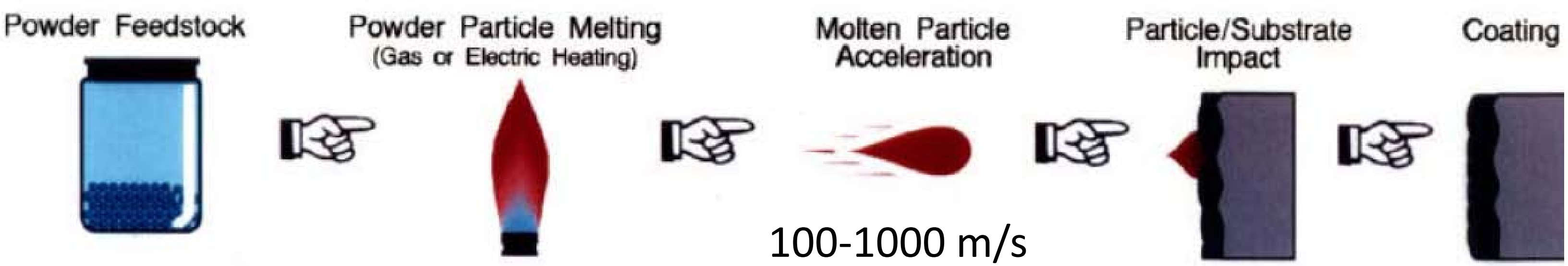
High pressure

- Industrial-scalable non-equilibrium synthesis



What is Thermal Spray?





100-1000 m/s

um to cm

Protective Coating → Electronics and Sensors

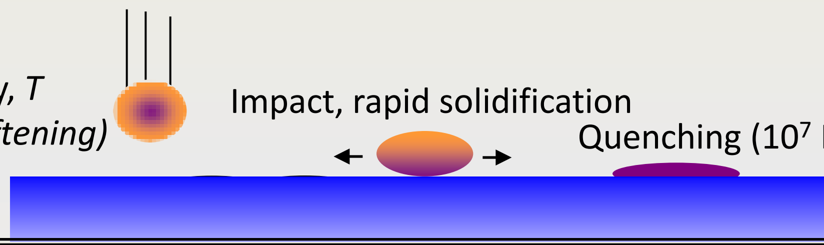
Sanjay Sampath (co-PI), Thermal Spray Applications in Electronics and Sensors: Past, Present, and Future, Journal of Thermal Spray Technology, Vol 19, 2010

Thermal Spray: Non-Equilibrium Processing

Melting, quenching and consolidation in single process

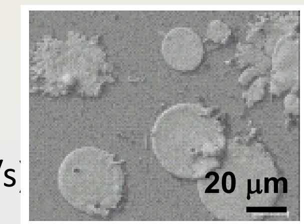
Splat based build-up and state induced properties

High velocity, T
(melting/softening)



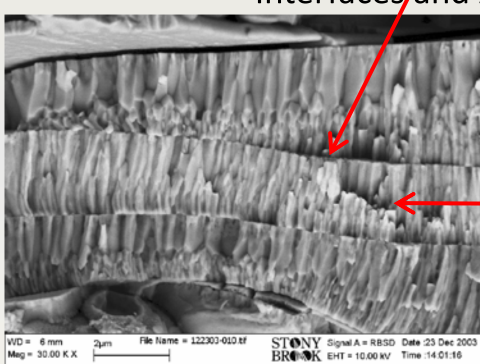
Impact, rapid solidification

Quenching (10^7 K/s)

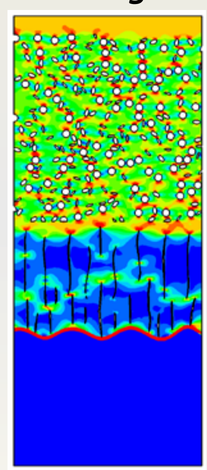


Layered and graded architectures through successive splat quenching

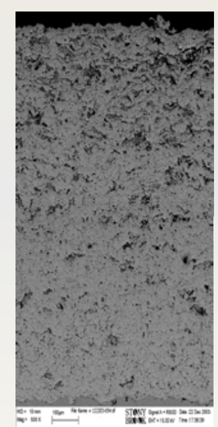
Interfaces and Adhesion



Micro Features and Phases



Layered Thick Films



Graded Porosity

Past Work: Thermal Spray of Iron Silicide
in Japan and Germany

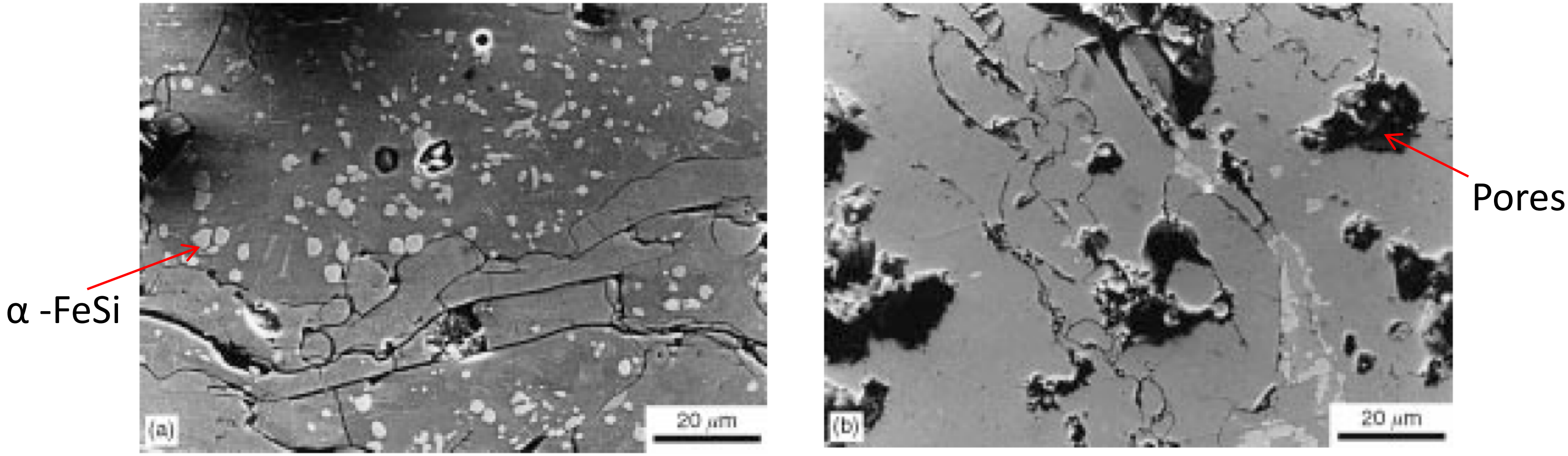
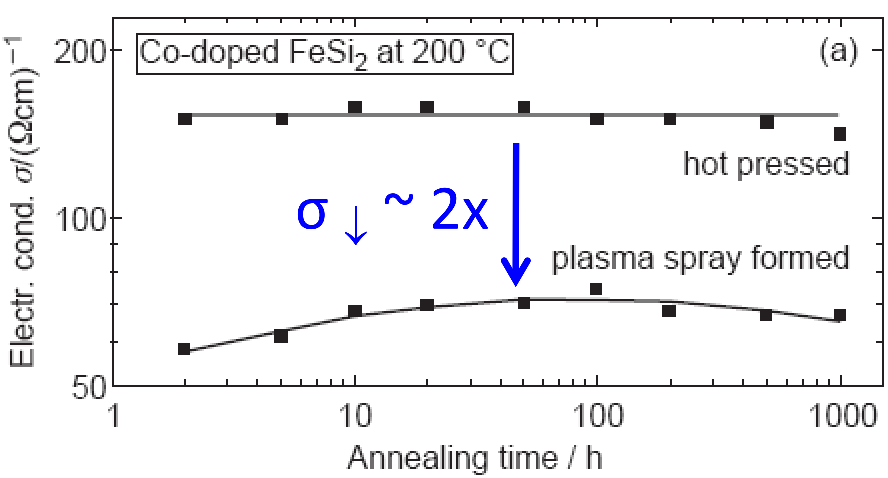
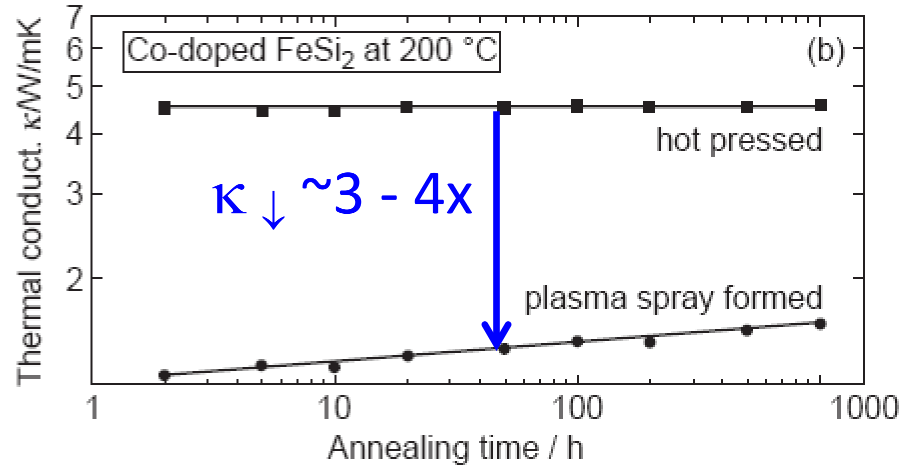


Figure 2 SEM of shrouded plasma spray (SPS)–formed iron disilicide: (a) as sprayed; (b) after 100 h heat treatment at 800 °C.

- A. Tsutsum, K. Kuramoto, et al, Structural design of large size Thermoelectric Module and Thermoelectric Properties of β-FeSi Prepared by Thermal Spraying, 17th Intl. Conference on Thermoelectrics, 1998
- J. Schilz. E. Muller, et al, On the thermoelectric performance of plasma spray formed iron disilicide, J of Material Science Letter, 17,1998
- J. Schilz, M. Riffel, et al, Plasma spray forming as a novel production method for thermoelectric materials, 15th Intl. Conference on Thermoelectrics, 1996

TE Properties of $FeSi_2$: Thermal spray vs. hot pressing





Seeback coefficient *S* almost the same

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

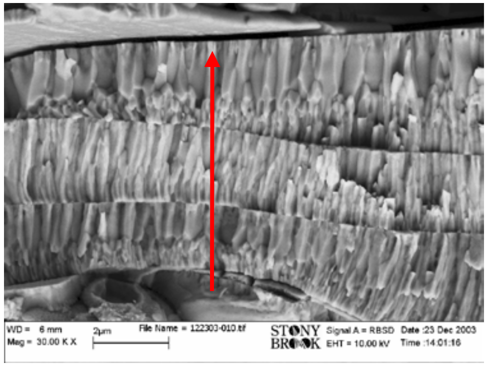


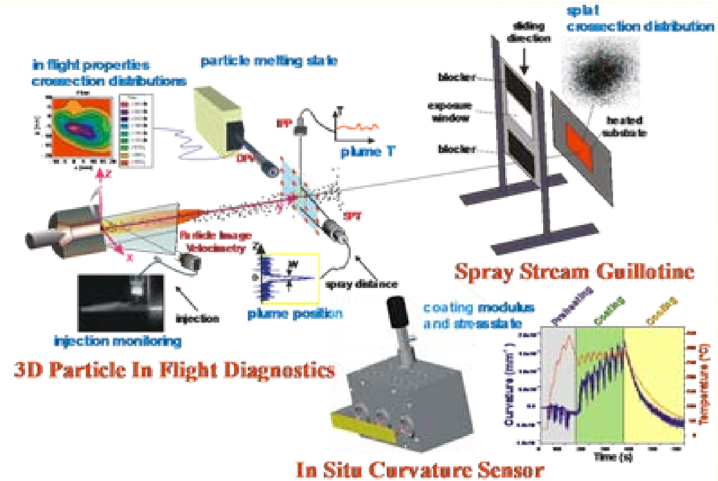
Figure of merit ZT increased by 30-60%!

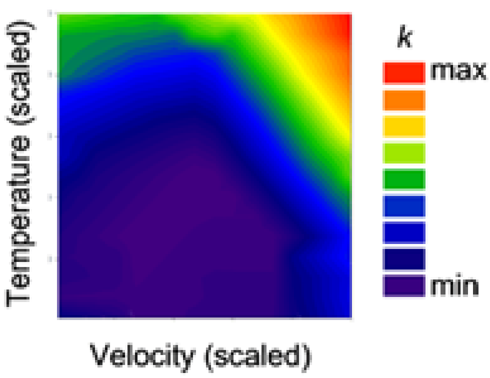
Center for Thermal Spray Research at SBU

Atmospheric Plasma Spray System
Sulzer Metco F4

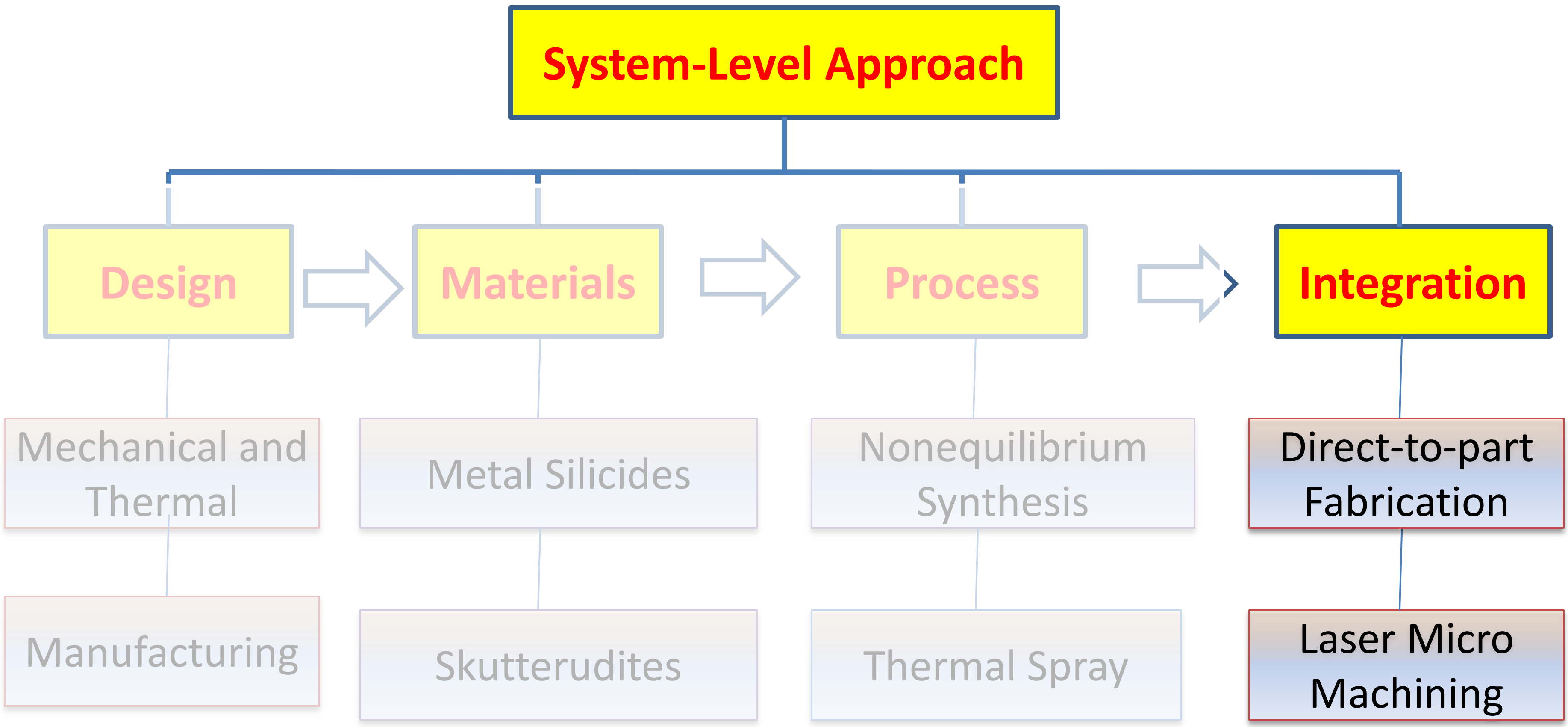
Consortium is operated by the Center for Thermal Spray Research at Stony Brook University

High Velocity Oxy-Fuel System
Sulzer Metco Diamond Jet (DJ-2600)

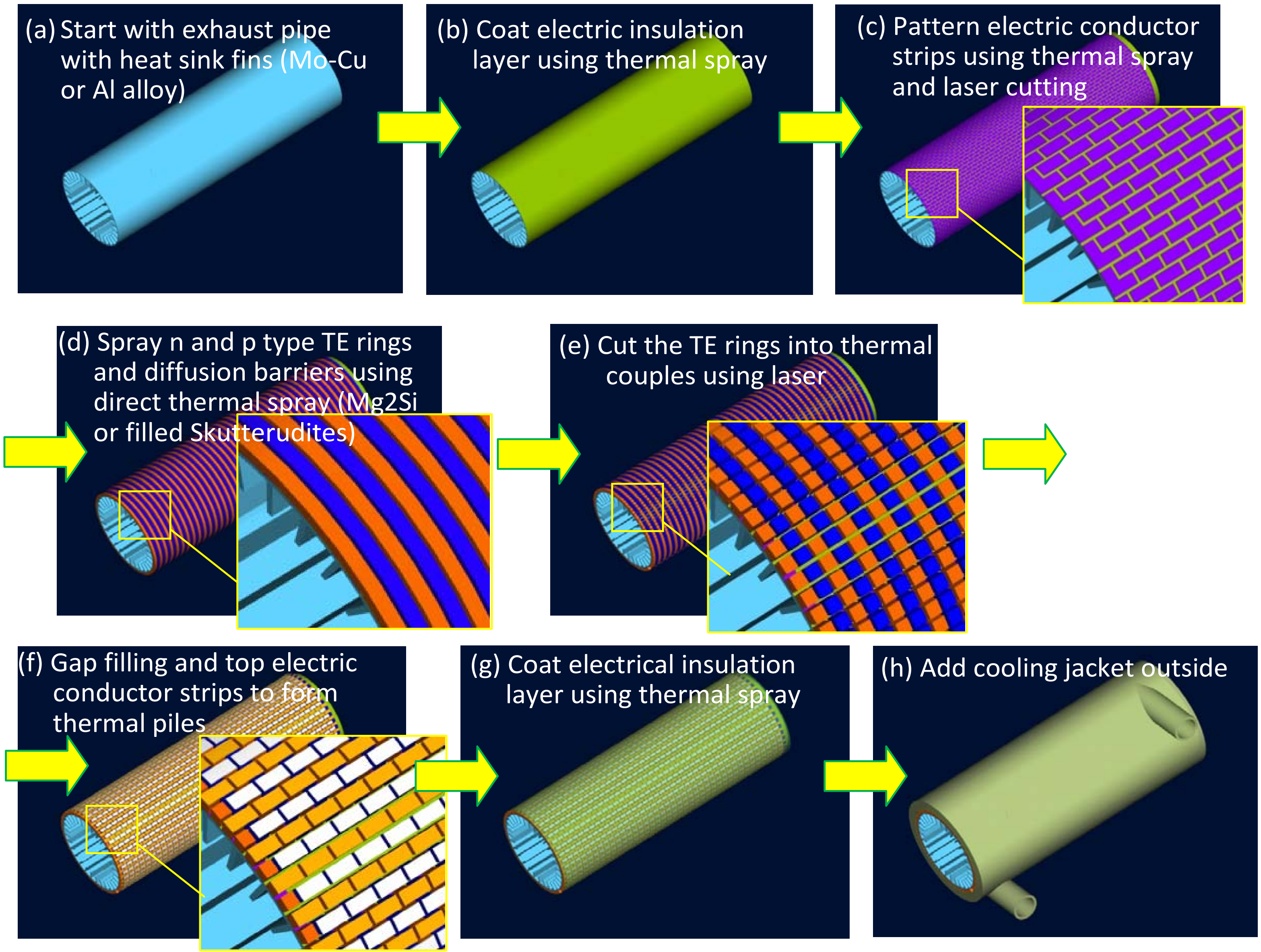




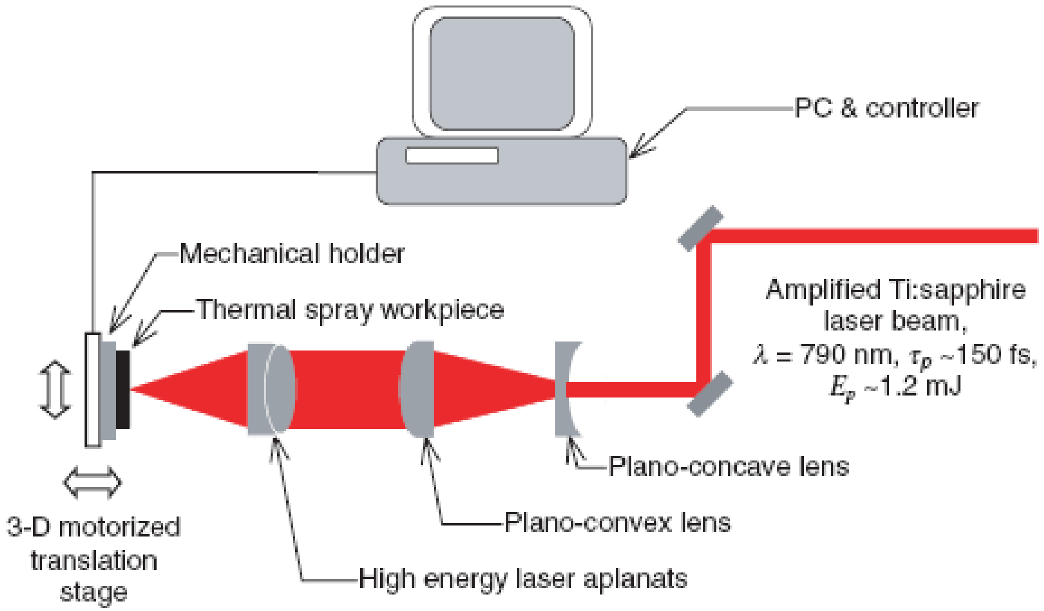
→ Integrated Design and Manufacturing

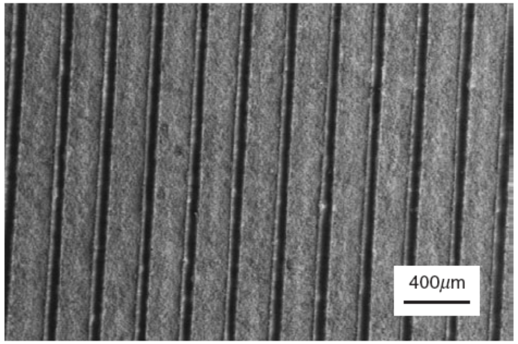


Integrated Design and Manufacturing

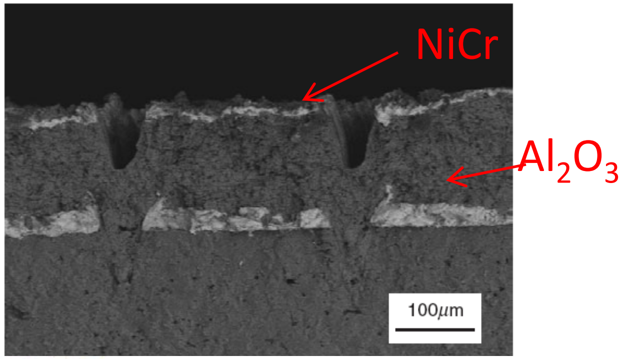


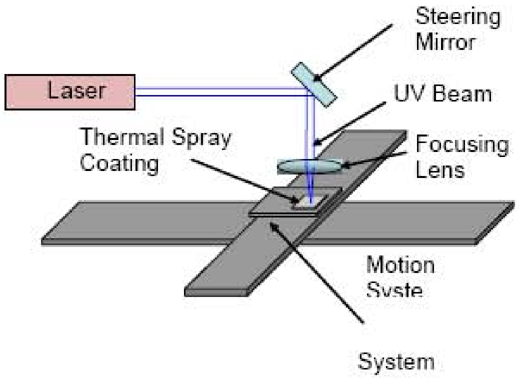
Short-Pulse Laser Micromachining

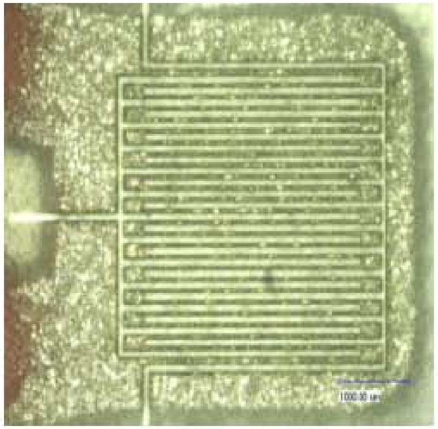


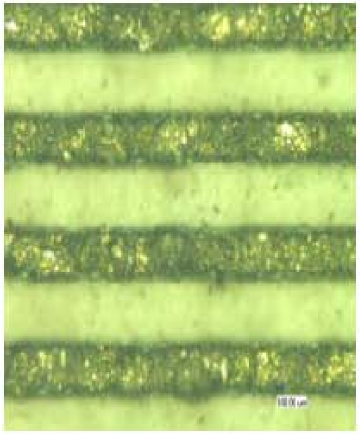


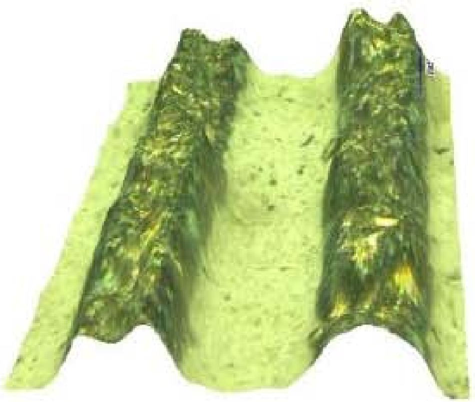
(a)



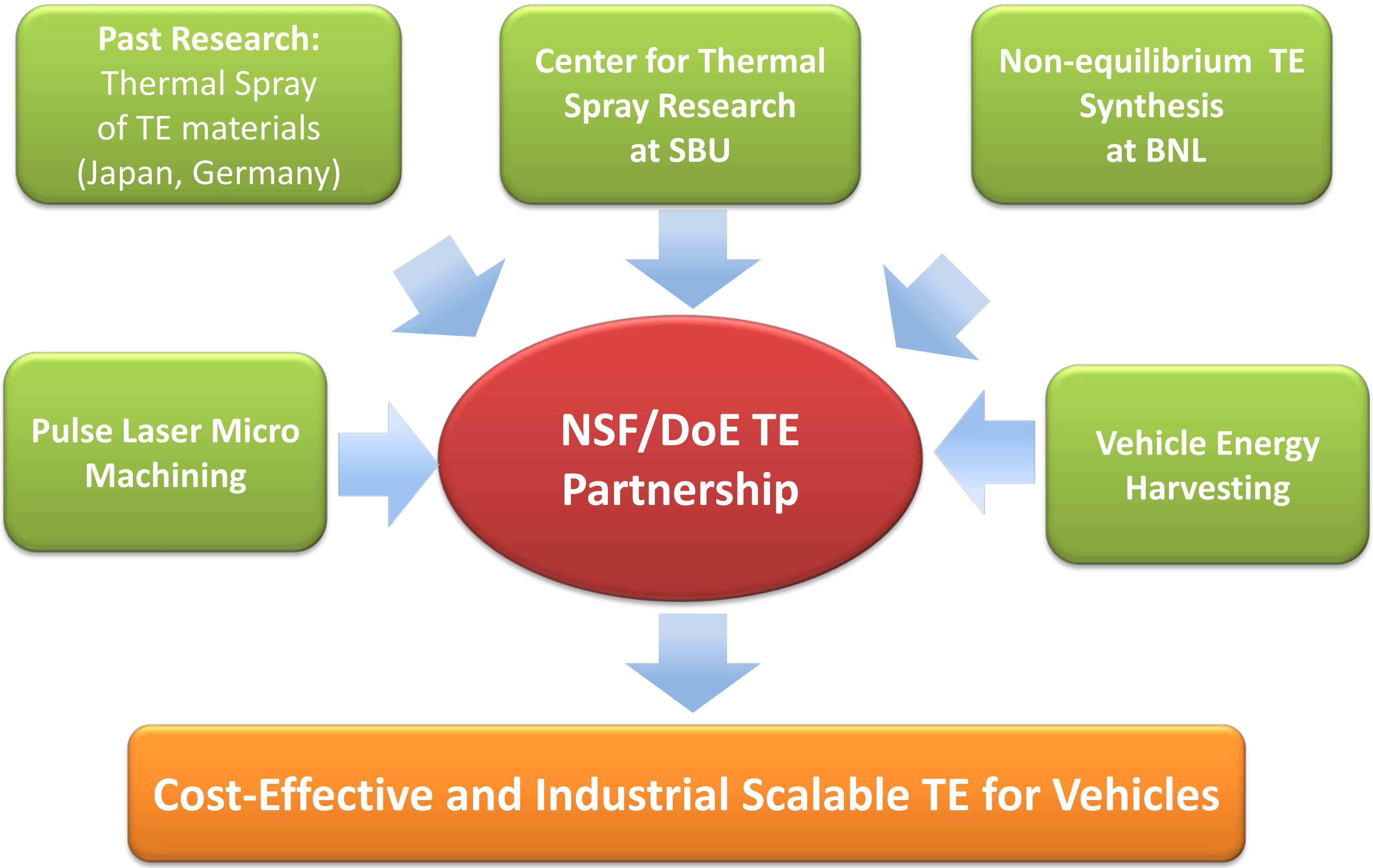






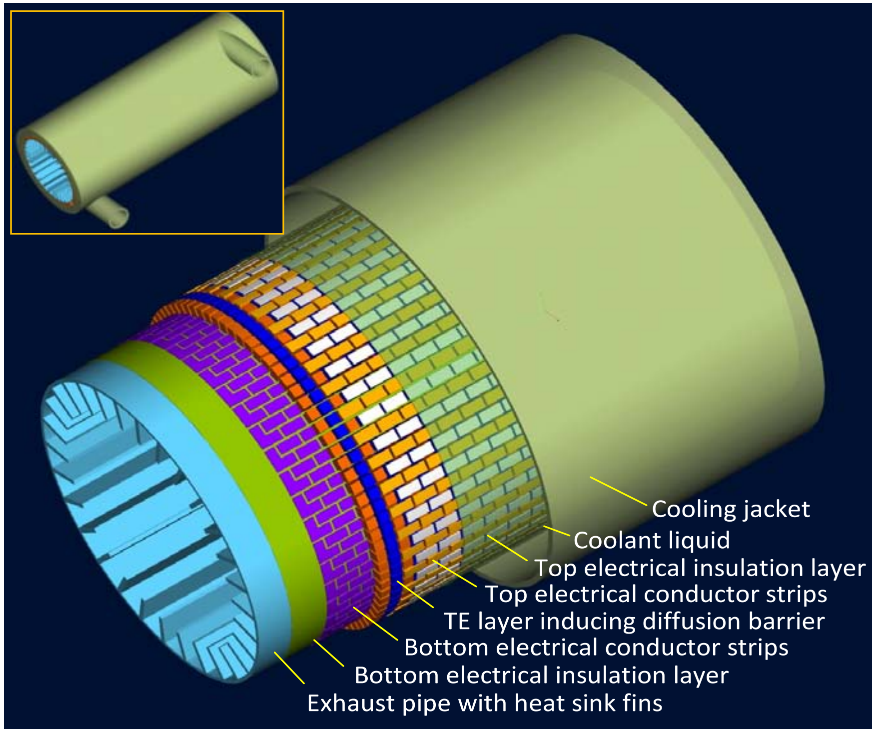


Prior Work and Resources



Summary

- *Systems-driven* approach to practical TE devices for vehicles
- *Non-equilibrium* synthesis of abundant, low-cost TE materials
- Integrated *direct-to-part* fabrication on exhaust pipe components using thermal spray and laser micromachining
- High-throughput, low-cost scalable manufacturing process



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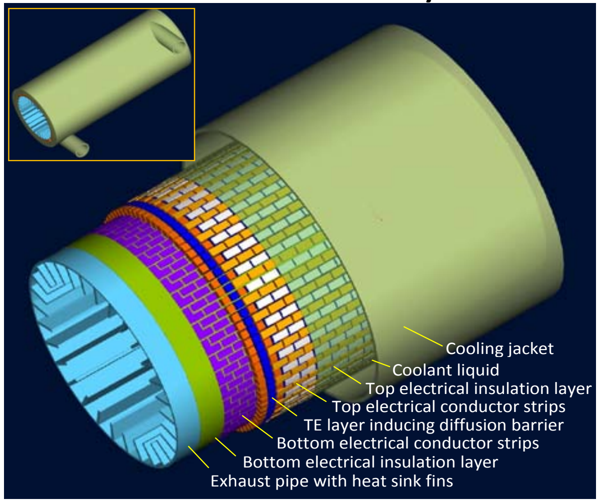

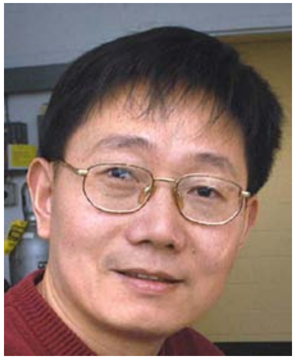

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