Mo-Si-B Alloy Development

J. H. Schneibel

Metals and Ceramics Divison, ORNL

R. O. Ritchie, J. J. Kruzic

Materials Science Division, LBNL

17th Annual Conference on Fossil Energy Materials
Baltimore, MD, April 22-24, 2003.

Why Ultra-High Temperature Materials?

Vision 21 is about **EFFICIENCY**:
Service temperature ↑ Efficiency ↑

Nickel-base superalloys: ≤ 1000ºC
ODS ferritic steels: up to 1400 º C
(but low strength and high stress exponent)

Need ultra-high temperature, high strength materials
Best effort, high risk research
Long lead time from research to production (20 years)

Applications: sensor protection, heat exchangers, 1st stage vanes

Ultra-High Temperature Materials

Barriers:

- Melting point
- Oxidation resistance
- Fracture toughness
- Creep strength

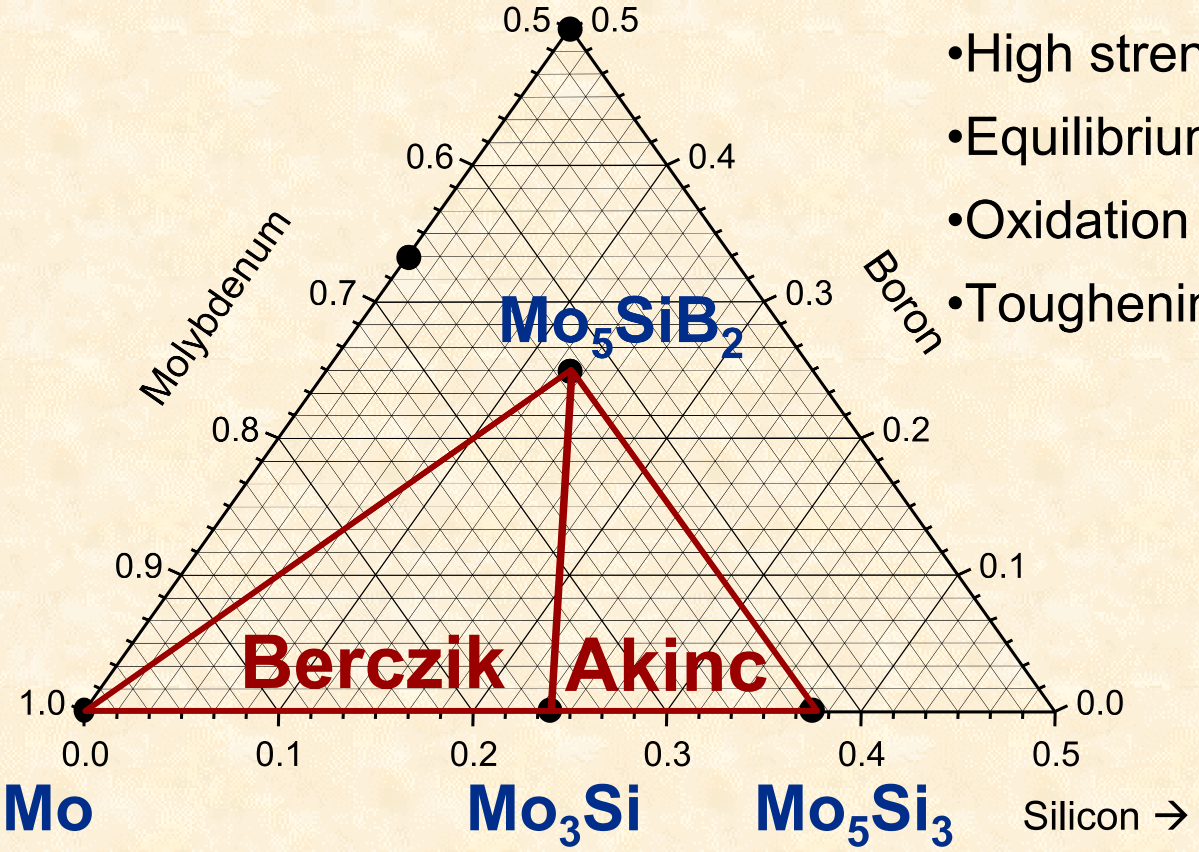
Options:

- Simple crystal structures – expensive (Pt, Ir)
- Complex crystal structures – brittle

Scientific approach:

macro- and microalloying
Innovative processing to create optimum microstructure

Why Mo-Si-B Alloys?



- Melting point ≈2000ºC
- High strength intermetallics
- Equilibrium phases
- Oxidation resistance: $MoSi_2$
- Toughening: metallic Mo phase

Mo-Si-B alloys are finding interest

Molybdenum-Borosilicide Workshop
Organized by Airforce, Navy, Pratt&Whitney
Annapolis, Maryland, March 11 and 12, 2003

TMS Symposium “Beyond Nickel-Base Superalloys”
Charlotte, NC, March 14-18, 2004

Strategy for improving the mechanical properties of Mo-Si-B Intermetallics

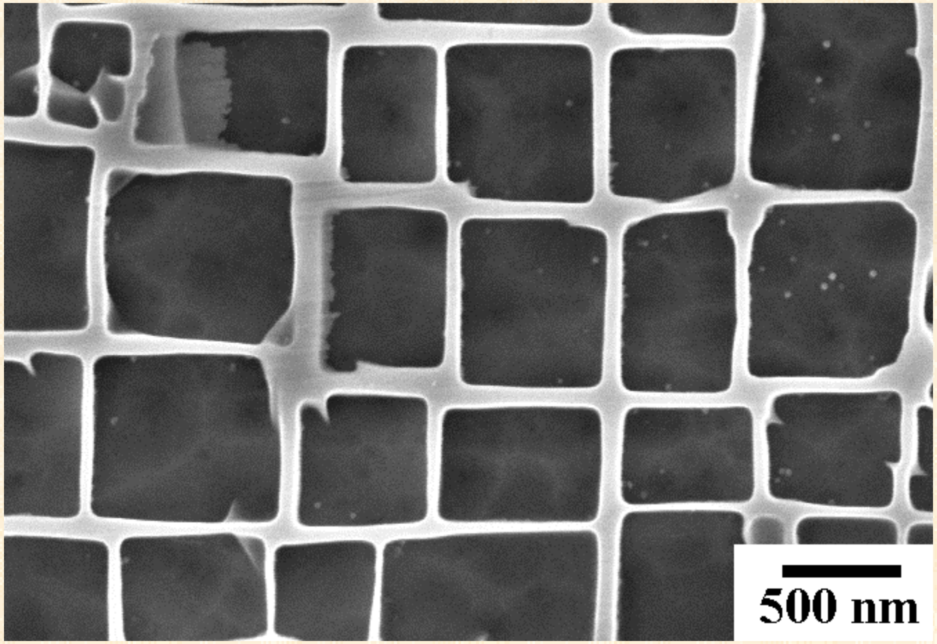
Unlikely that intrinsic brittleness of Mo_3Si and Mo_5SiB_2 can be alleviated in the near future

Engineer microstructure to minimize detrimental effect of brittle phases

Focus of this talk on:

- Microstructure topology and scale
- Mechanical properties of α-Mo

A sucessful microstructure for creep: nickel-base superalloys



CMSX-4

Single crystal superalloy

(Kazim Serin, Post-Doc at ORNL)

Continuous γ solid solution matrix

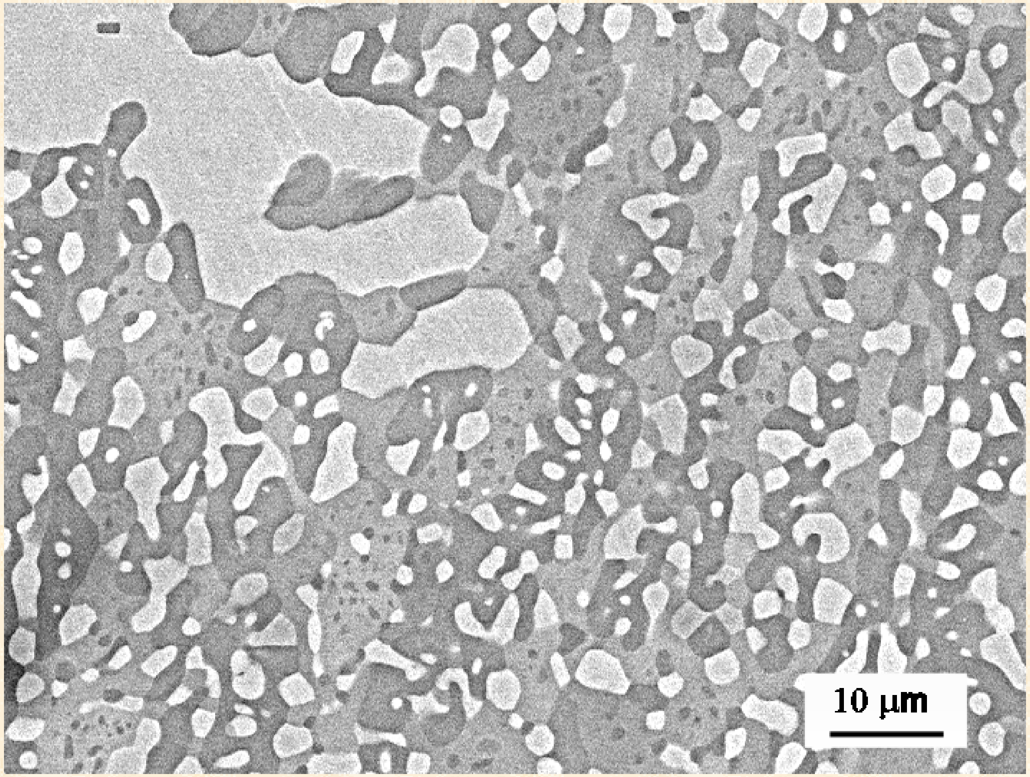
Creep occurs in the γ channels

between γ' (Ni_3Al) precipitates

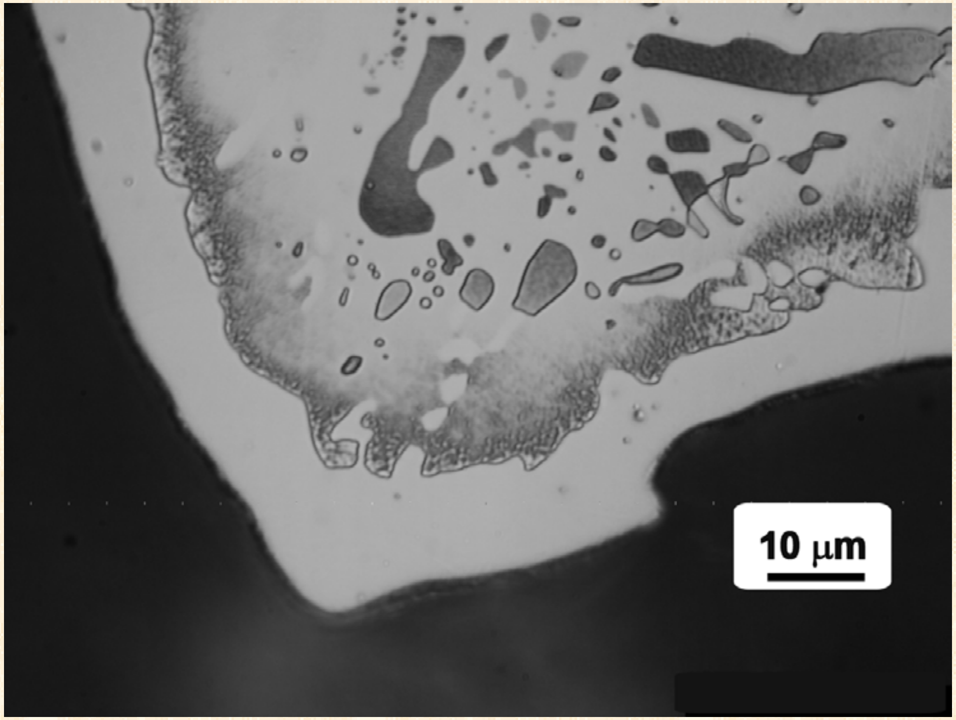
Optimizing Fracture Toughness

- High α-Mo volume fraction
- Continuous α-Mo
- Coarse α-Mo

Mo-12Si-8.5B (at. %)
cast&annealed (24h/1600ºC)
≈40 vol. % discontinuous α-Mo



Crush cast Mo-Si-B and “coat” powder with Mo



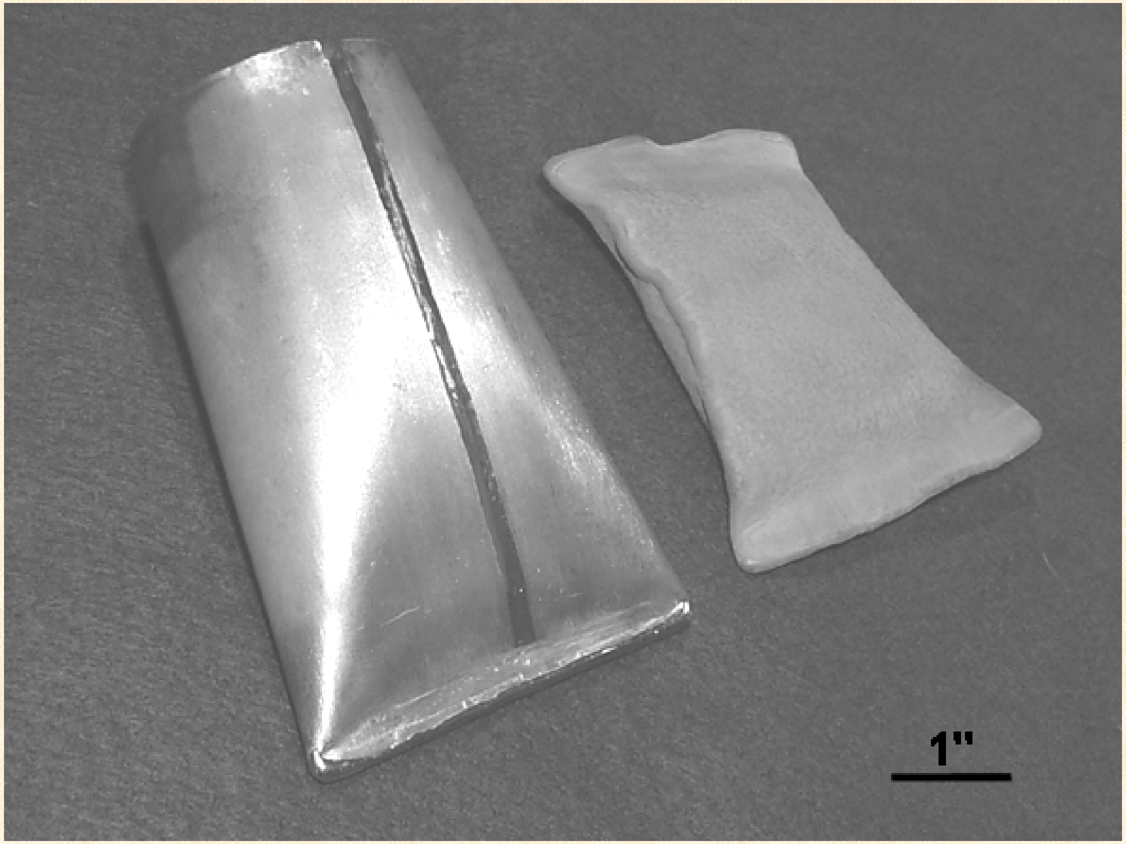
Mo-20Si-10B powder particle after 16 h at 1600°C in vacuum

Evaporation of Si and/or:

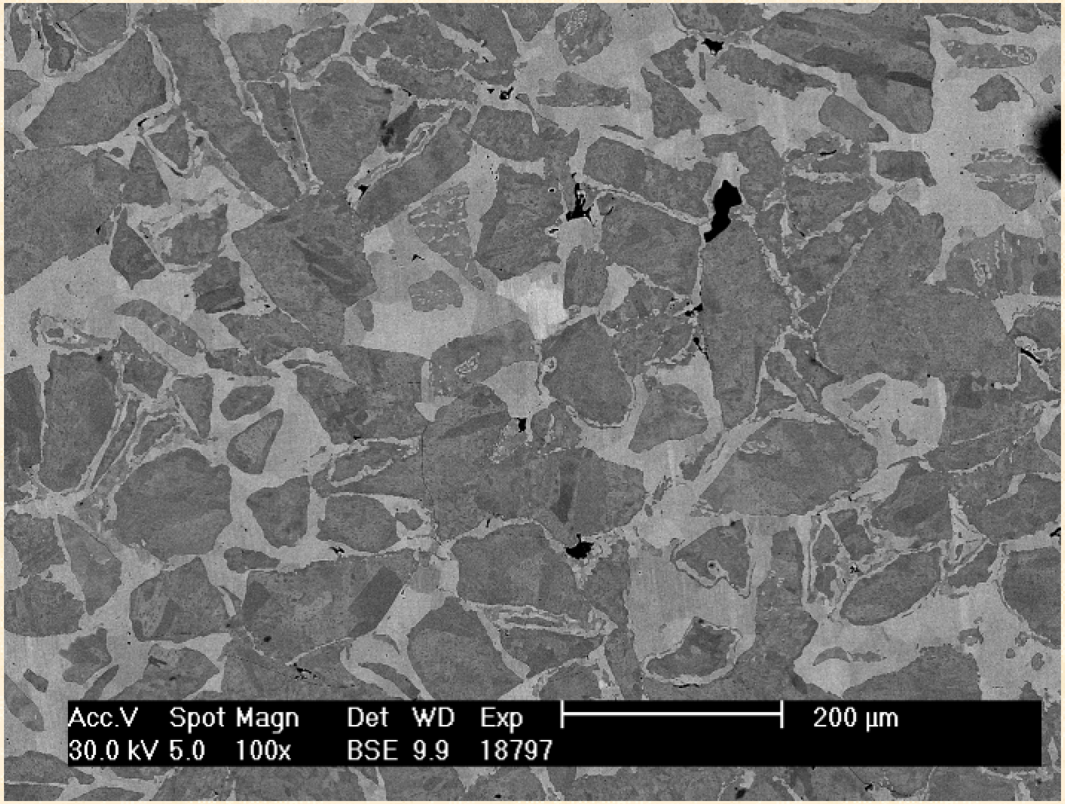
$Mo_3Si + 1/2O_2 \rightarrow SiO\uparrow + 3\ Mo$

$Mo_5SiB_2 + 1/2\ O_2 \rightarrow SiO\uparrow + 2\ Mo_2B + Mo$

Hot isostatic pressing of Mo-Si-B powder in niobium can (4h/1600°C/30ksi)



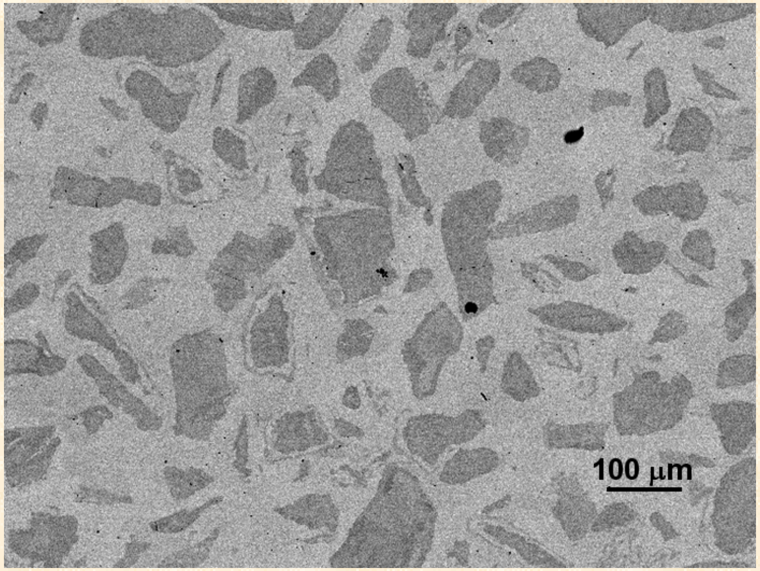
HIPed Mo-Si-B with continuous α-Mo matrix: nominal composition Mo-15Si-10B; 30 vol.% α-Mo.



Mo-Si-B alloys with continuous α-Mo HIPed from Si-evaporated Mo-20Si-10B

Specimen Designation	Powder size prior to Si semoval	α-Mo volume fraction, %
Fine	≤ 45 μm	34
Medium	45-90 μm	34
Coarse	90-180 μm	49
Medium_Low	45-90 μm	5

Tensile Testing of Buttonhead Specimens at 3.3×10^{-3} s^{-1}



“Coarse” microstructure
Continuous α-Mo matrix
49 vol. %

Room temperature:

premature fracture at 140 MPa:
Need to eliminate flaws
Mo matrix needs improvement

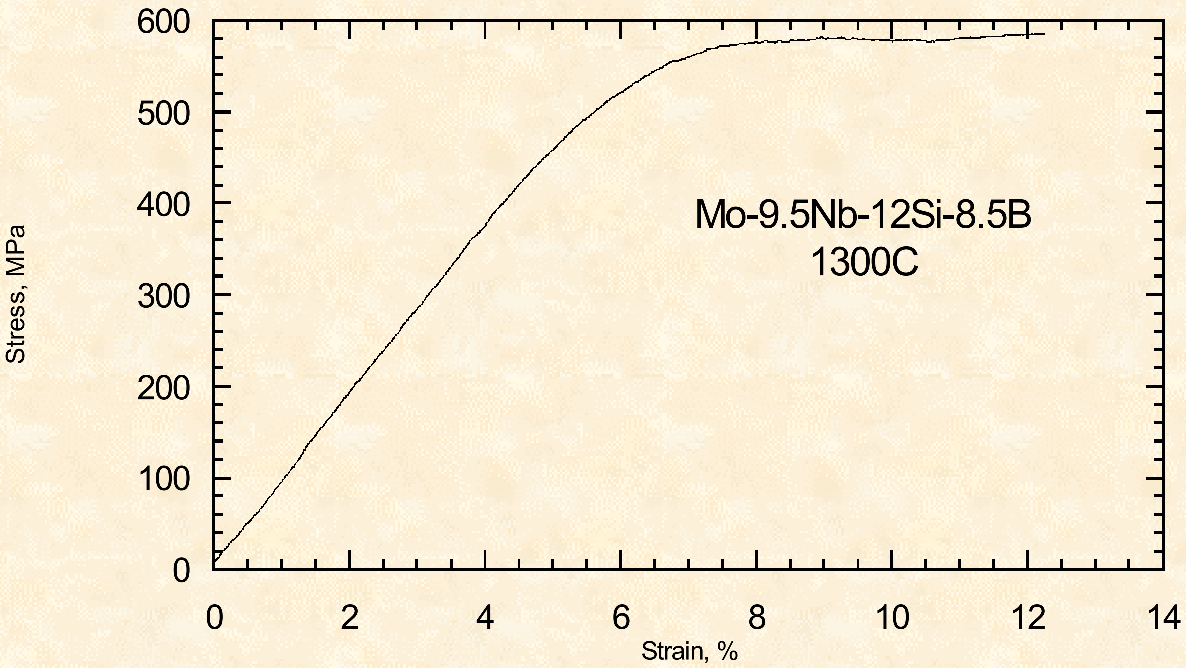
1200ºC in vacuum:

0.2% yield stress	336 MPa
maximum stress	354 MPa
ductility	1.8%

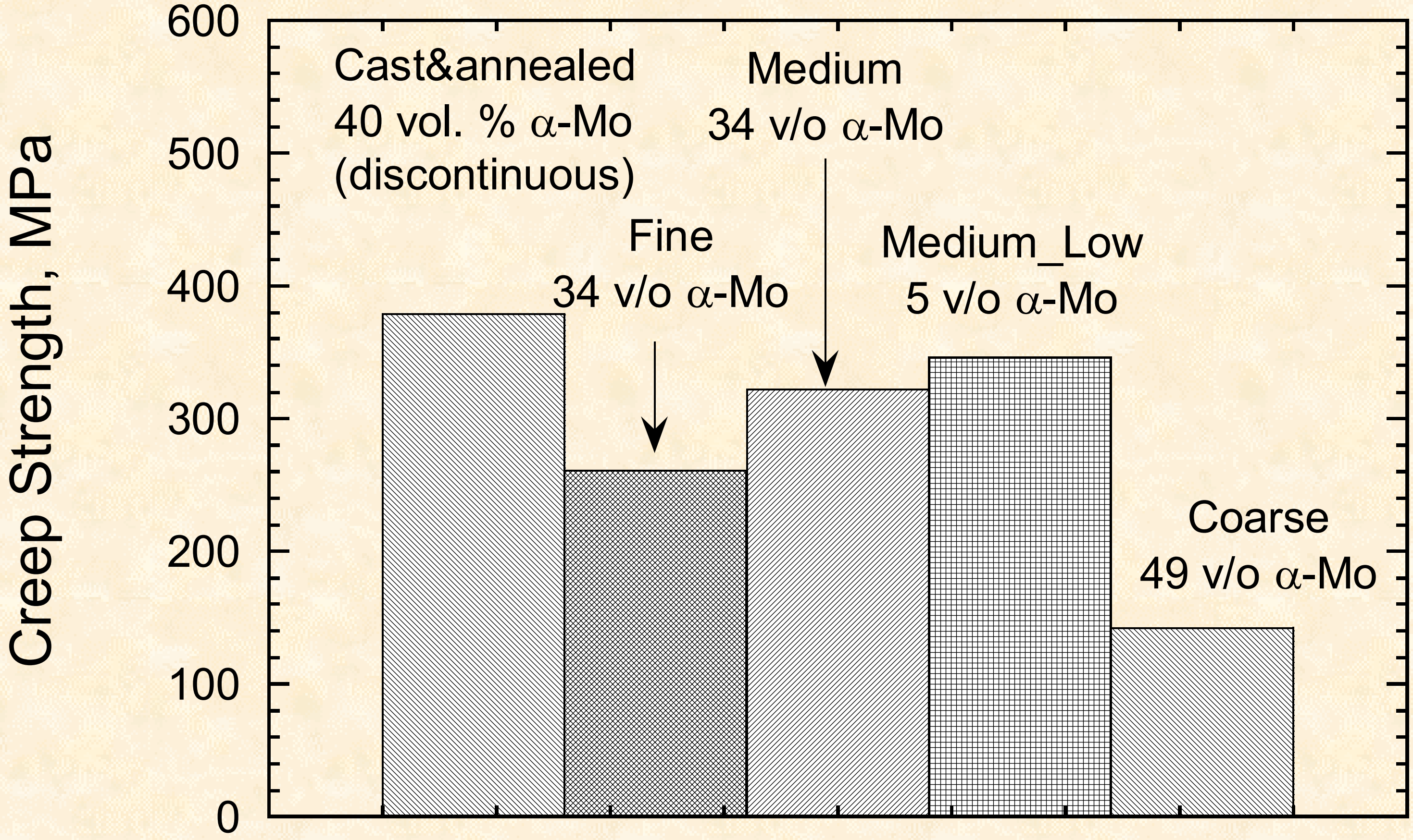
Creep strength

Determine compressive stress-strain curves at a strain rate of 10^{-5} s^{-1}

Define creep strength as flow stress at 2% plastic strain



Creep Strength at 1300°C (10^{-5} s^{-1}, 2% plastic strain)



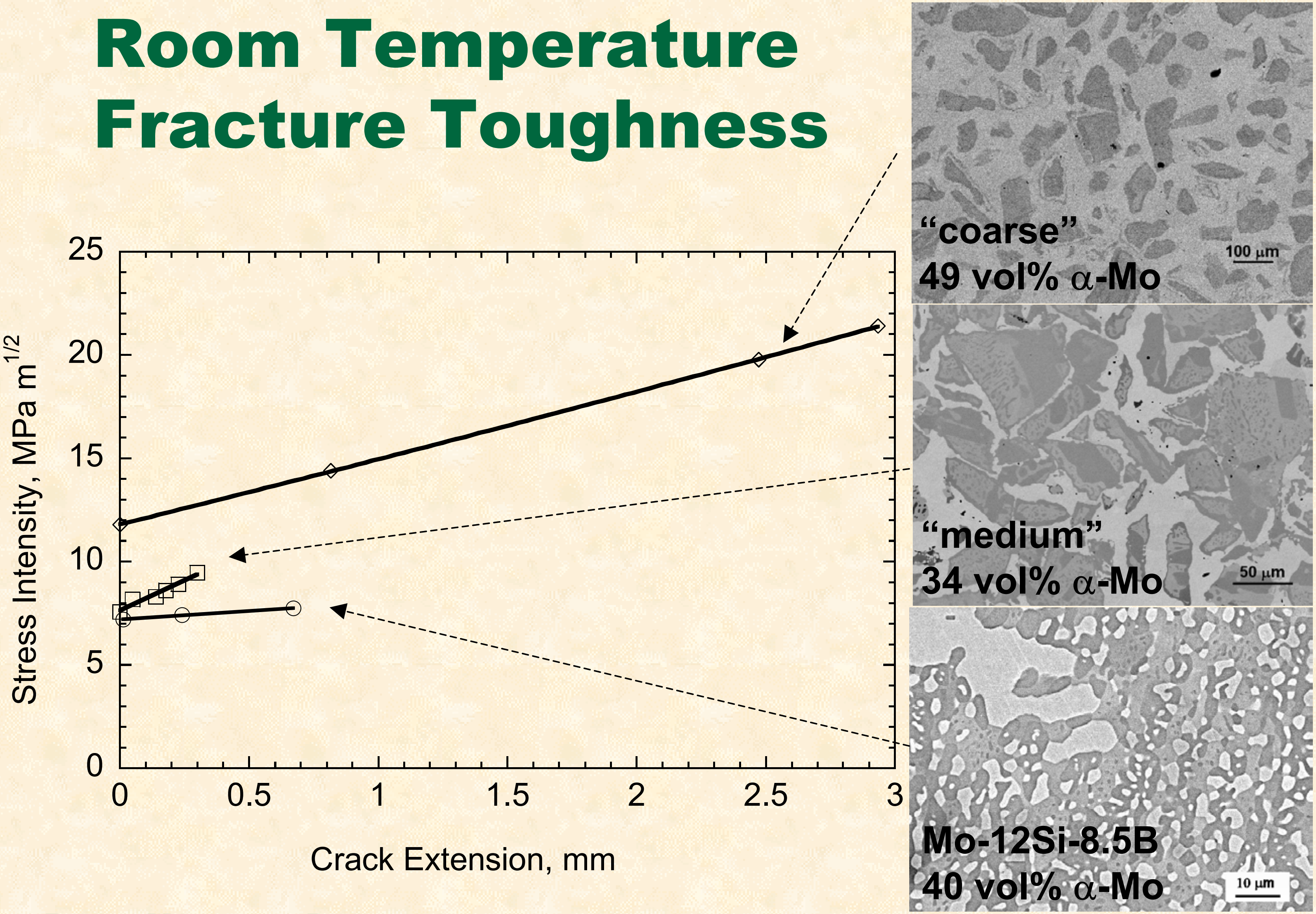
Rigorous Fracture Toughness Testing

- Disc-shaped compact tension specimens
- Fatigue pre-cracking
- Cycling at low stress intensity:

  remove bridging in crack wake
- Crack length from elastic compliance
- Determine resistance curve (*R*-curve)

  (Crack-growth resistance K_R vs. crack extension Δa

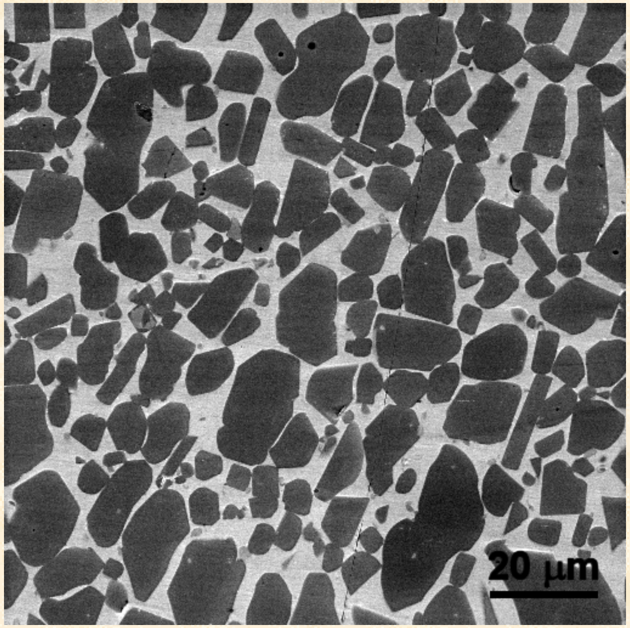
Room Temperature Fracture Toughness



What can we do to improve toughening efficiency of α-Mo? High toughening efficiency → less α-Mo, better oxidation resistance

- α-Mo ligaments < 1 μm
- Microalloying of α-Mo
- Ductilization of α-Mo by spinel particles

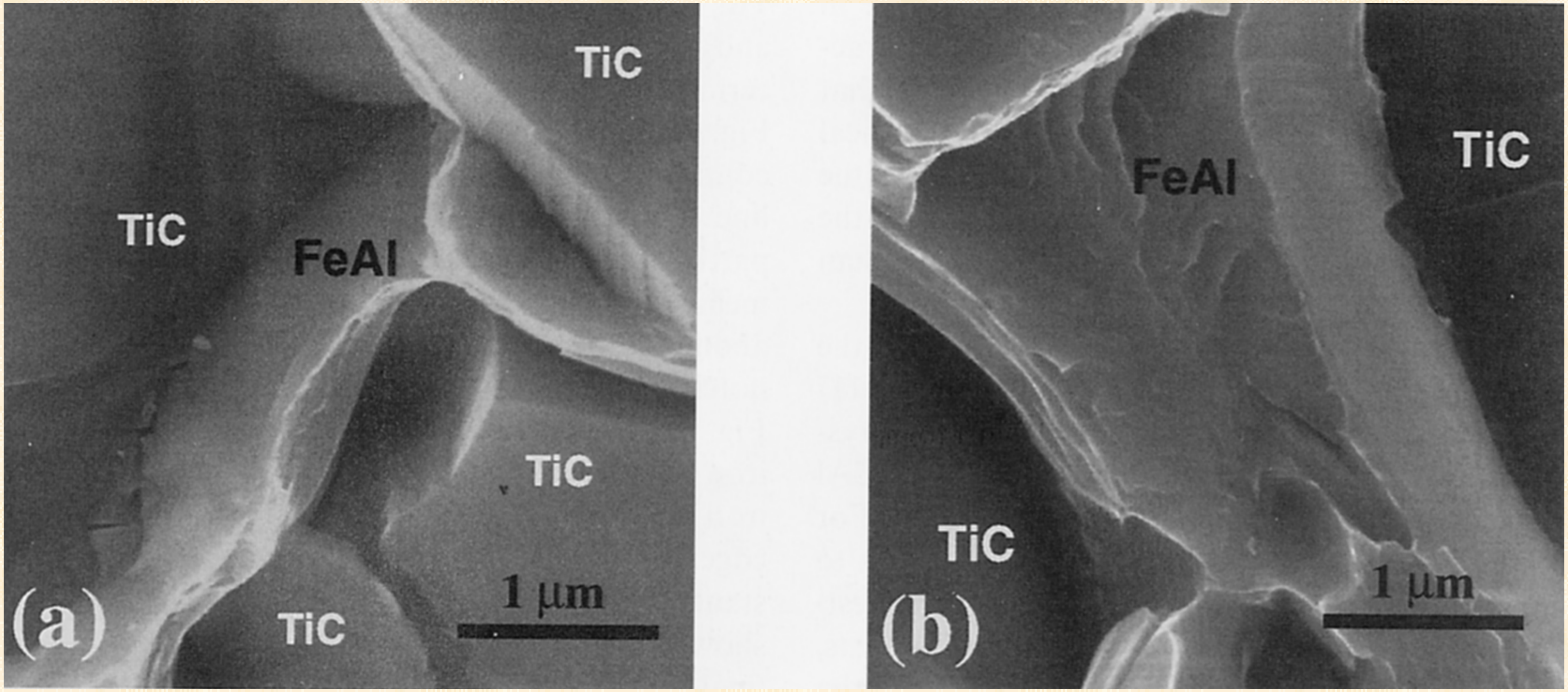
  (Mike Brady: chromium)



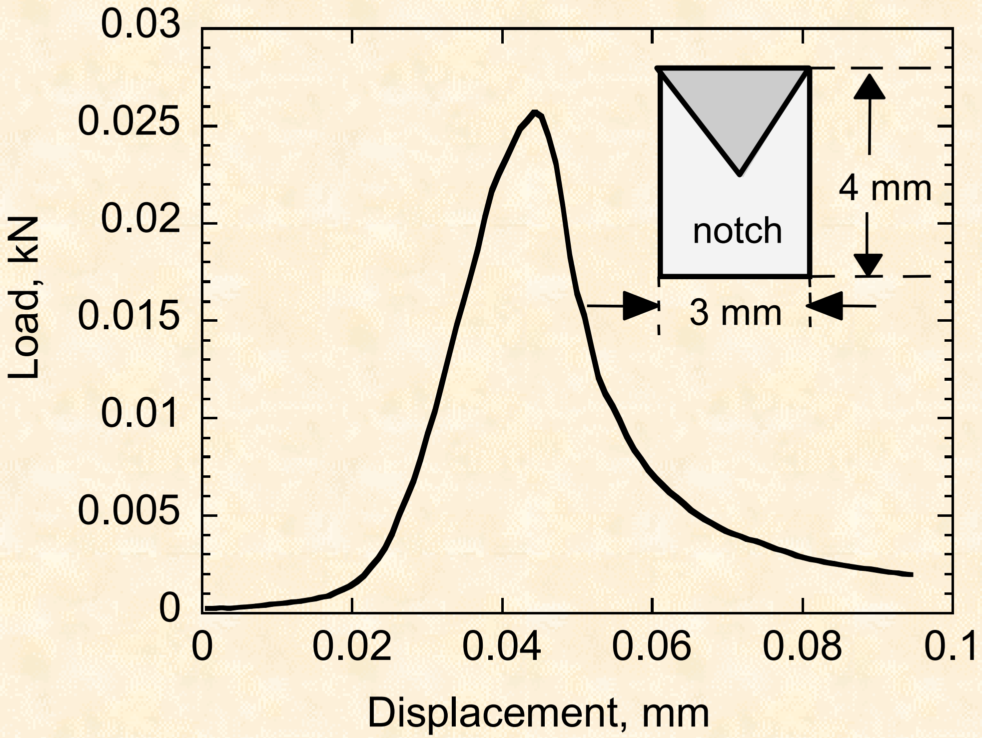
Fe-40 at. % Al/TiC:
FeAl fractures usually by cleavage;
Fracture mode of FeAl ligaments depends on thickness

Fracture stress of FeAl ligament: 500 MPa
1 dislocation in pile-up: $L=Gb/[\pi\tau(1-\nu)]=30$ nm
70 dislocations in pile-up: ideal cleavage stress for L=2 μm
Expect ductile fracture for ligaments < 2 μm

FeAl ligaments show ductile fracture for thickness less than 2 μm: Size scale important for fracture toughness



Additions of Ti and Zr improve the ductility and strength of Mo (→TZM): Try this approach with Mo-Si-B alloys



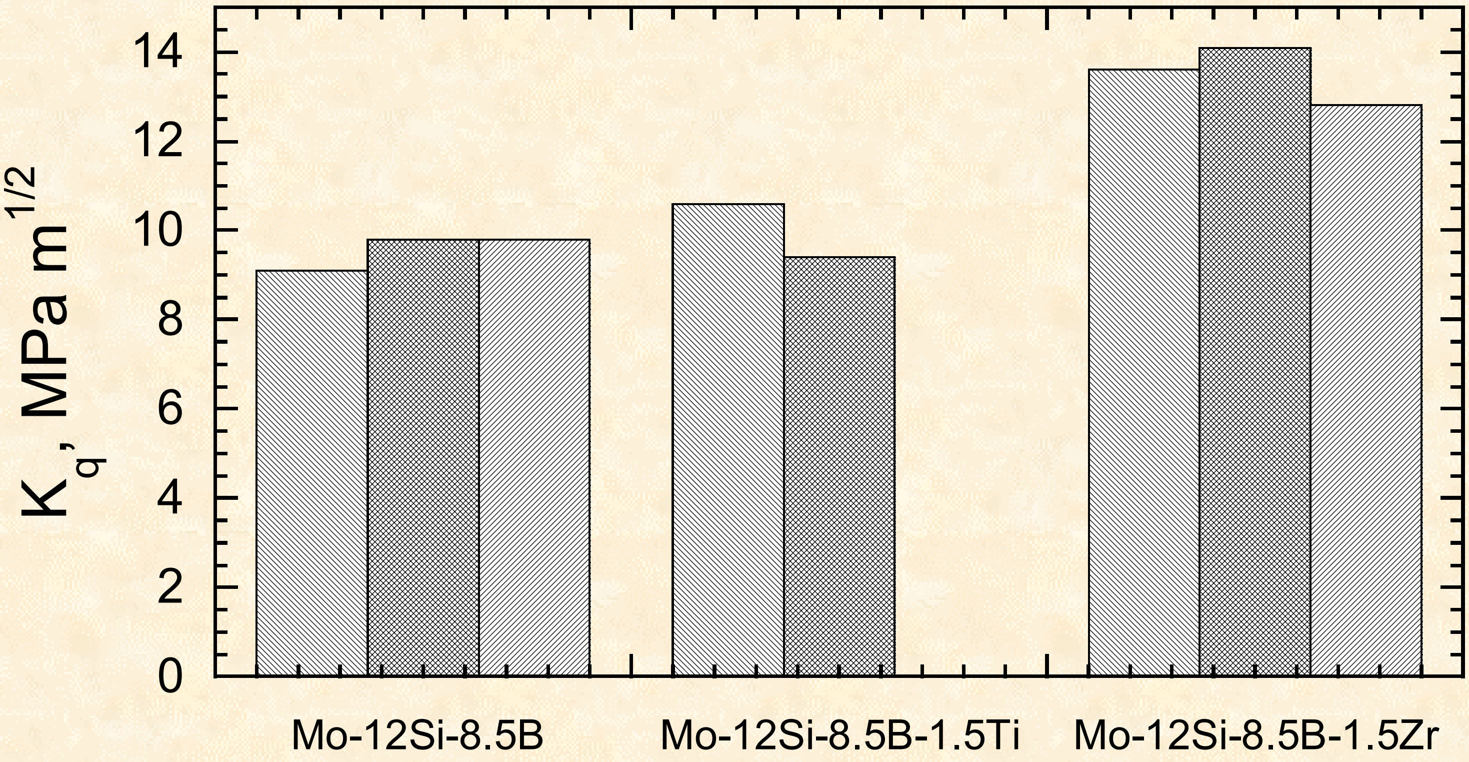
Screening tests:

Flexure tests with chevron-notched specimens

$G=W/A$

$K_q=[(E\times G)/(1-\nu^2)]^{1/2}$

Zr additons improve room temperature fracture toughness, probably by improving properties of α-Mo



Ductilization of Mo by adding spinel particles ($MgAl_2O_4$)

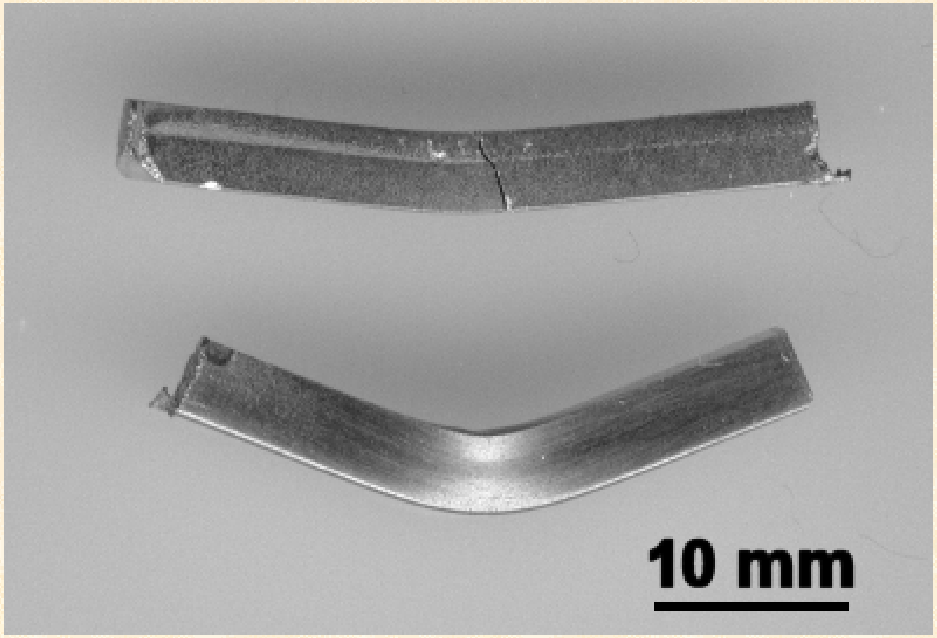
M. P. Brady recently revisited the Scruggs mechanism (1965) for the ductilization of Cr by spinel particles

Scruggs showed that mechanism works for Mo as well

Consolidate Mo powder (2-8 μm) and 3.4 wt% $MgAl_2O_4$ spinel powder (1- 5 μm) in graphite hot-press: 4h/1800°C/20MPa/vacuum

Carry out room temperature flexure tests

Ductilization of molybdenum by spinel particles ($MgAl_2O_4$)



Optimum particle size and volume fraction?
Collaboration with Bruce Kang, WVU

Summary and Conclusions

- Processing of Mo-Mo_3Si-Mo_5SiB_2 with continuous α-Mo matrix
- Control of microstructural scale and α-Mo volume fraction
- Limited tensile ductility at 1200C
- Qualitative correlation between microstructure and creep strength
- High room temperature fracture toughness & *R*-curve behavior
- Zr microalloying additions improve fracture toughness
- Spinel particles improve ductility of Mo

Future work:

Continue to focus on the mechanical properties of α-Mo phase