A Potential Seal for High Temperature Applications Based on Niobium Oxide – Aluminum Oxide

Phase I Contract DE-FG26-05NT42537

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UCR Contractors Review Conference, Pittsburgh, PA
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Outline

- Background and Motivation
  - Colorado School of Mines energy focus
  - Observations Nb/Al_2O_3 composites
  - Why would Nb_2O_5/Al_2O_3 lead to a glass?
- Objectives
- Experimental plan
- Results to date
- Conclusion

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The State of Colorado recently established the Colorado Fuel Cell Center (CFCC)

The CFCC builds on the strong foundation of ongoing collaborations

TDA Research

NREL

ITN Energy Systems Inc.

Versa Power Systems

School of Mines 1874 Colorado

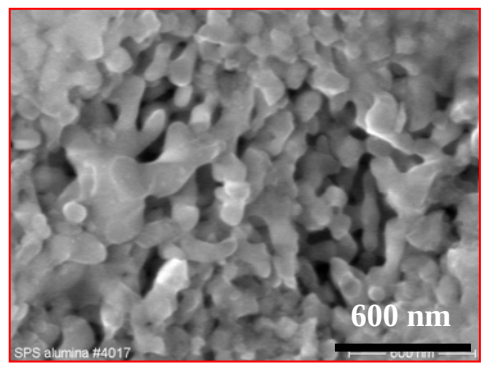
CoorsTek Amazing Solutions.

Mesoscopic Devices
Precision solutions for a shrinking world

School of Mines 1874 Colorado

New Materials Needs for High Temperature Separation Processes

- Gas separation (H_2, CO, CO_2, CH_4 and H_2O)
  - Molecular sieves (microporous materials)
  - Atomic or ionic transport (dense metallic or ionically conducting membranes)
  - High temperature requirements (e.g., for H_2 separation processes)
    - Micro- or nano-porous alumina
- Sealing components
  - High temperature requirements
  - Hermeticity



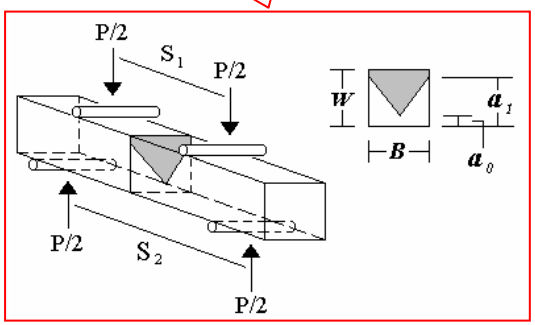
Porous alumina (SPS) from Dr. J. Shen, Arrhenius Laboratory, Stockholm Sweden

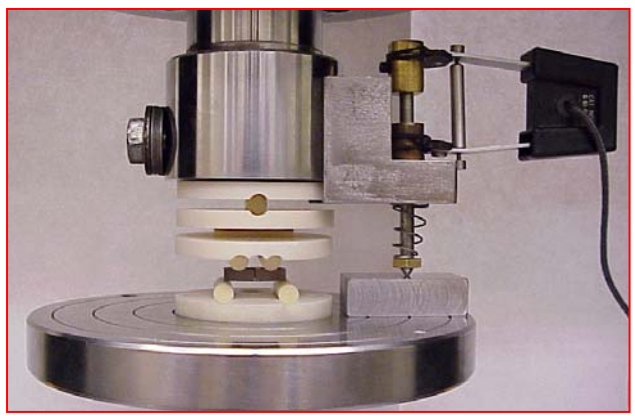
Observations in Nb/Al_2O_3 Composites

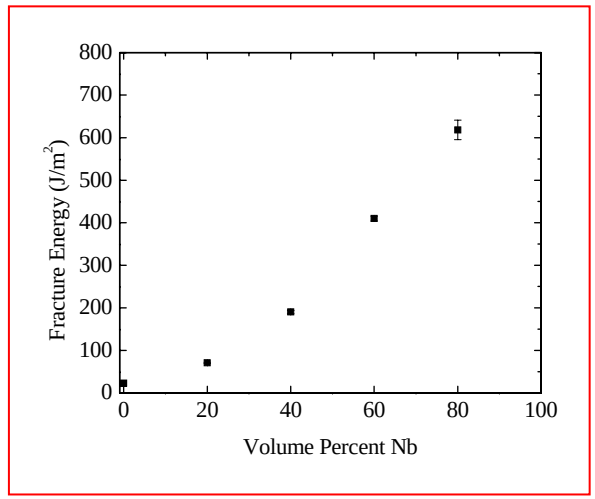
- Fundamental study on fracture in layered, graded composites (Funded by ARO)

Powder Metallurgy – Hot Press

Volume % Nb	Volume % Al_2O_3
20	80
40	60
60	40
80	20







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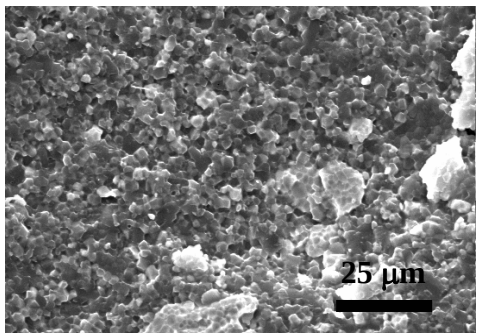
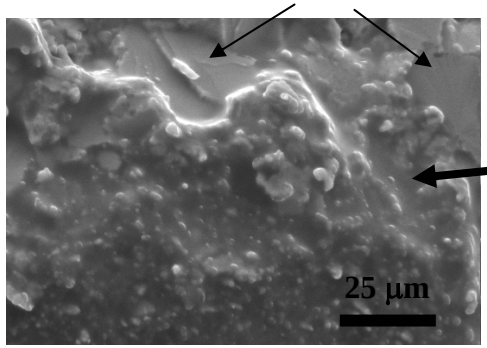
Why is Composite Toughness Low?

- Reason: a brittle glassy phase formed in the microstructure



20 vol. % Nb



60 vol. % Nb

Secondary phase coats Al_2O_3 and has amorphous traits

Why Would Niobium Oxide/Aluminum Oxide Form a Glass?

- Nb_2O_5 is a conditional glass former (will form a glass in the presence of certain oxides)*
  - Liquidus temperature effect (low liquidus = low thermal energies → will not break bonds as readily
  - 2nd oxide may modify the melt structure
  - Cations likely do not mix well in structure

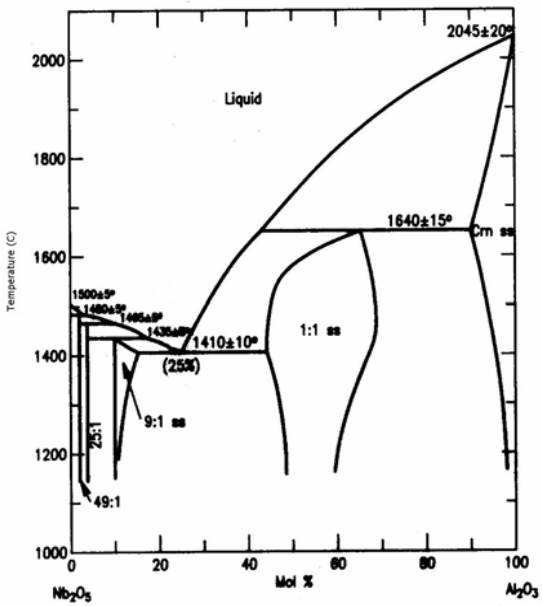
- New glass seal?
  - Could a niobium oxide/aluminum oxide based glass be used as a seal?
    - Thermal expansion mismatch low
    - Appears to wet alumina

* Has been applied as an amorphous semiconducting film

Applying this Observation

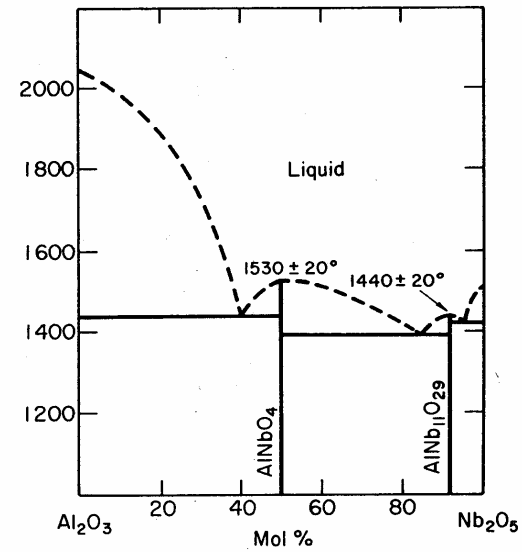
- Approach
  - Explore compositions of Nb_2O_5/Al_2O_3 where a glass may form – e.g., near eutectic composition

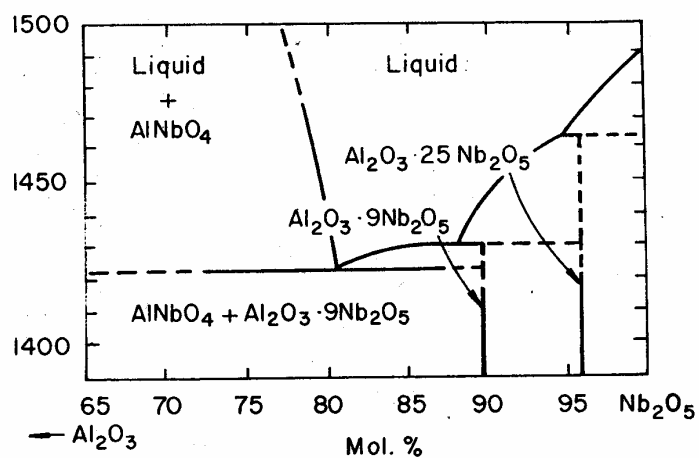
Which Phase Diagram is Correct?



A. Purdese, M. L. Borlera and P. Rolando, *Atti Accad. Sci. Torino, Cl. Sci. Fis. Mat. Nat.*, 99, 1079-1087 (1964-1965).

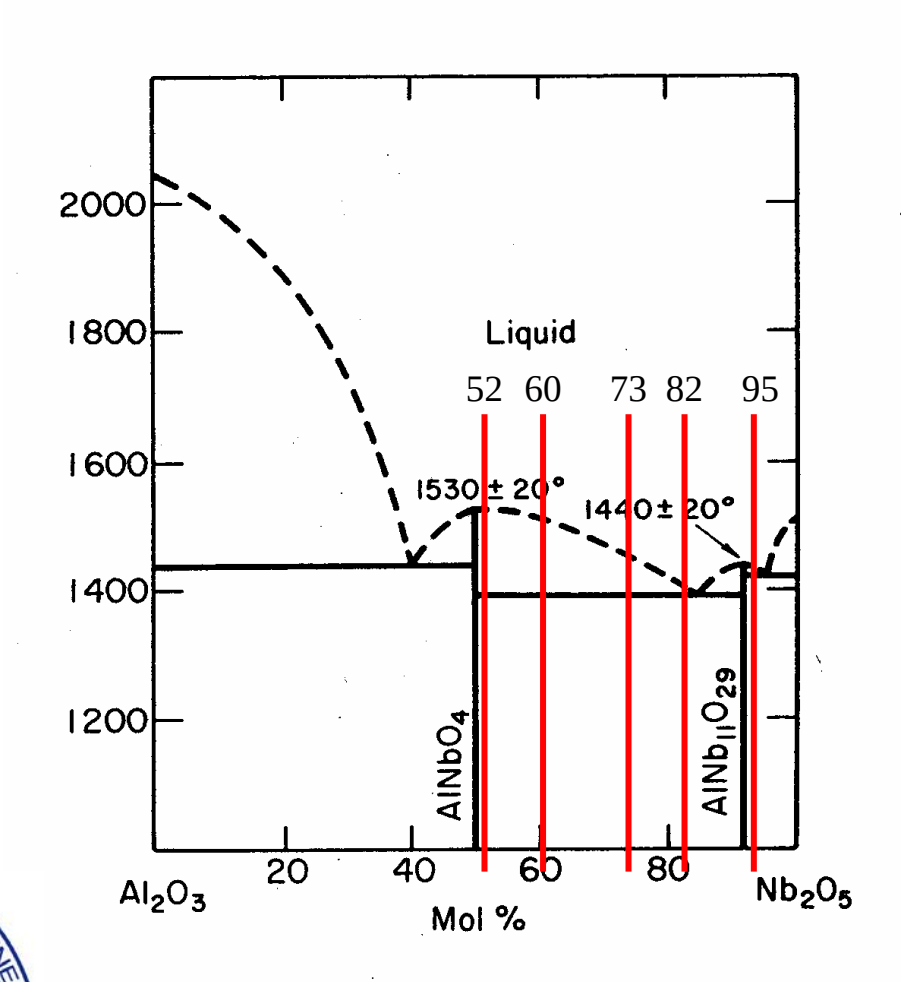
E. N. Isuprova, N. A. Godina and E. K. Keler, *Izv. Akad. Nav. SSSR, Neorg. Mat.*, 6[8] 1465 (1970); *Inorg. Mater. (USSR)* 6[8] 1292 (1970).





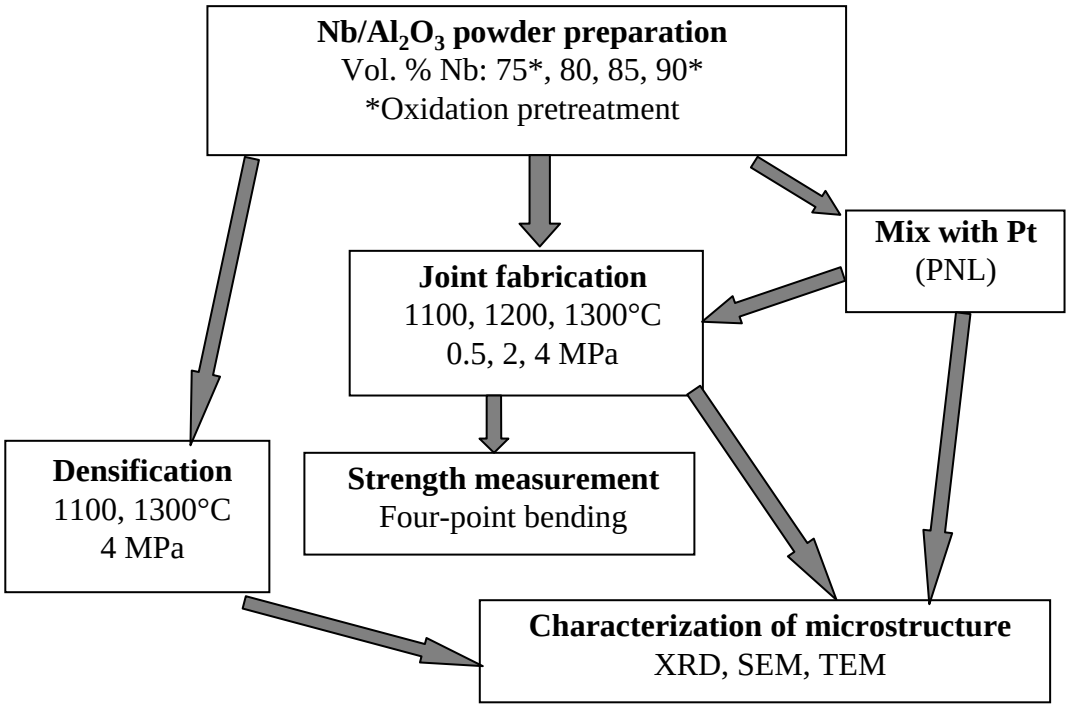
G. K. Layden, *J. Am. Ceram. Soc.* 46,[10] 506 (1963).

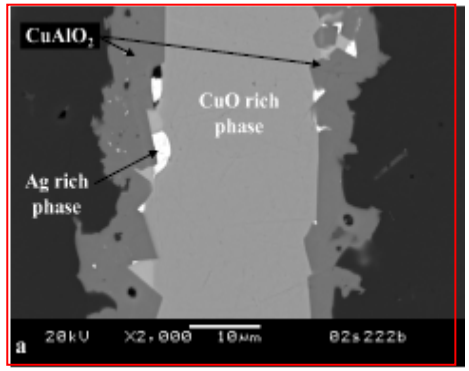
Objectives of Project



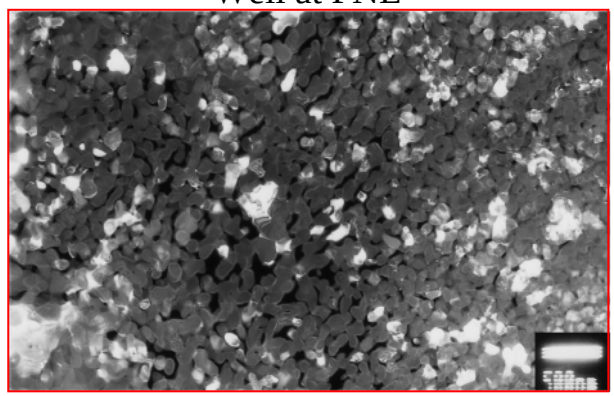
- Establish experimental conditions necessary to produce glassy phase
- Formulate compositions of greater than 50 mol % Nb_2O_5 (remainder Al_2O_3)
  - Examine with regard to wetting and reactivity
- Produce and mechanically test joints

Experimental Plan





SEM of reactive metal braze formed at 1100°C from Scott Weil at PNL



TEM of porous Al_2O_3 prepared by J. Shen and taken by T. Höche

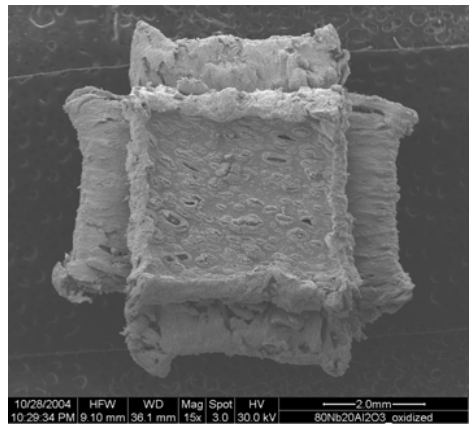
Three Specimen Fabrication Methods

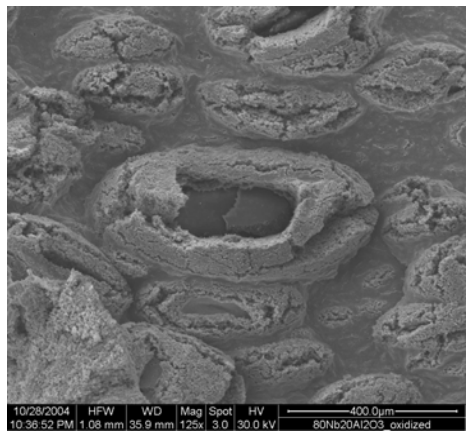
- Oxidation treatment of Nb/Al_2O_3 to form Nb_2O_5/Al_2O_3 followed by hot pressing
- Purchased Nb_2O_5: Hot pressing
- Purchased Nb_2O_5: Cold pressing/sintering

Some specimens were re-heated above the melting temperature and cooled quickly

Material Preparation - 1

- Oxidation treatments
  - Alfa Aesar Nb powder 99.8 % pure
  - CoorsTek Al_2O_3 powder 99.9% pure
  - Mix, oxidize (1300°C in air, 30 min)
- Hot pressing (1400°C, 1 hr, 4 MPa, vacuum)
- No glassy phase observed
- Lack of control over microstructure





Nb/Al_2O_3 composites oxidized 1100°C

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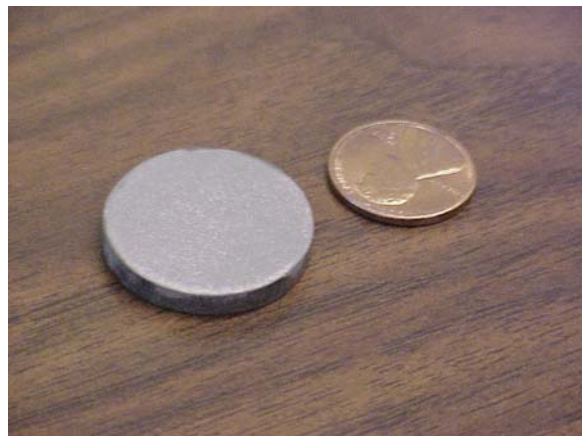
Material Preparation - 2

- Purchased powder Nb_2O_5 (Alfa Aesar) mixed with Al_2O_3 (high purity, CoorsTek)
- Hot pressed (1400°C, 1 hr, 4 MPa, vacuum)
- Selective specimens were re-heated to 1450°C in air and quickly cooled to attempt to form a glassy phase



Hot pressed Nb_2O_5-Al_2O_3 specimen

Material Preparation - 3

- Purchased powder Nb_2O_5 (Alfa Aesar) mixed with Al_2O_3 (high purity, CoorsTek)
- Cold pressed, sintered

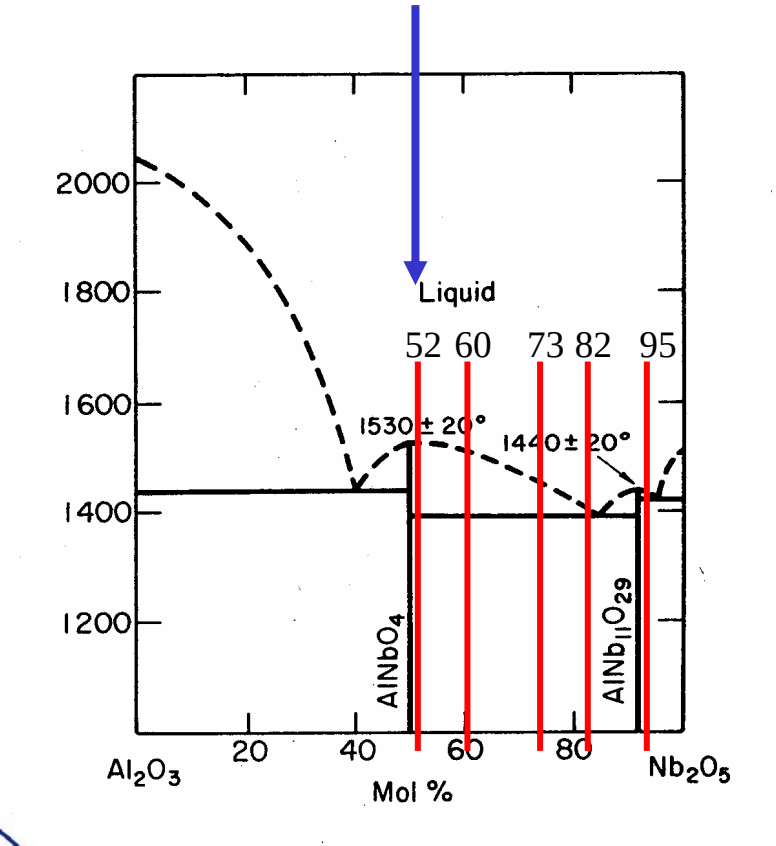
Cold pressed and sintered Nb_2O_5-Al_2O_3 specimen

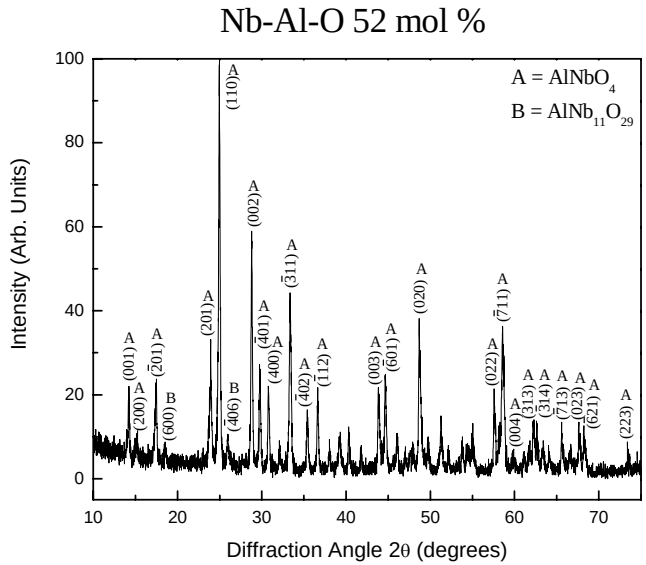
Results to Date

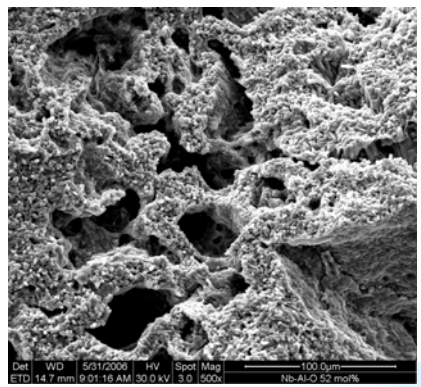
Composition (mol % Nb_2O_5)[1]	Processing Route[2]	XRD[4]	Visual Inspection	SEM
60	HP	$AlNbO_4$ and $AlNb_{11}O_{29}$	dark gray to black; coarse grained	no glass
75 wt. % Nb	HP[3]	NC	sliver with gray particles (Nb); porous	NC
82	HP	$AlNbO_4$ and $AlNb_{11}O_{29}$	dark gray to black; coarse grained	no glass
	furnace heat treatment of above specimen	$AlNbO_4$ and $AlNb_{11}O_{29}$	melted; light green color with white crystals	no glass
90 wt. % Nb	HP[3]	NC	silver with gray particles (Nb); porous	NC
52	CS	$AlNbO_4$ and $AlNb_{11}O_{29}$	shape change indicating creep; white, rough and porous	no glass
60	CS	NC	surface melted, whitish gray	NC
73	CS	$AlNbO_4$ and $AlNb_{11}O_{29}$	melted; coarse elongated crystals; whitish gray	no glass
95	CS, 1450ºC	NC	melted; glaze; coarse, elongated crystals; whitish-gray	NC

[1] unless otherwise indicated
[2] HP indicates vacuum hot pressed at 1300ºC.; CS indicates cold pressed and sintered at 1420ºC unless otherwise indicated.
[3] indicates that these specimens were prepared by pre-oxidizing the Nb to form Nb_2O_5.
[4] NC indicates not completed yet.

52 mol % Specimen







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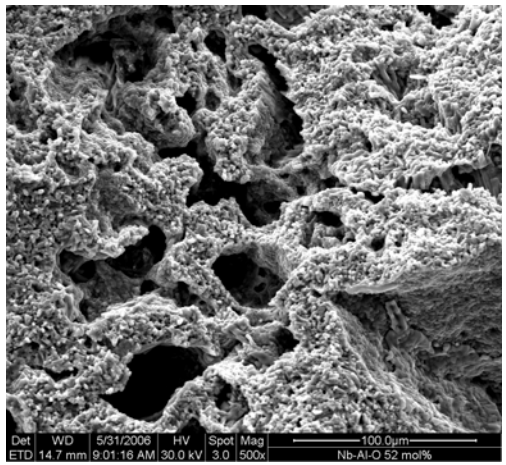
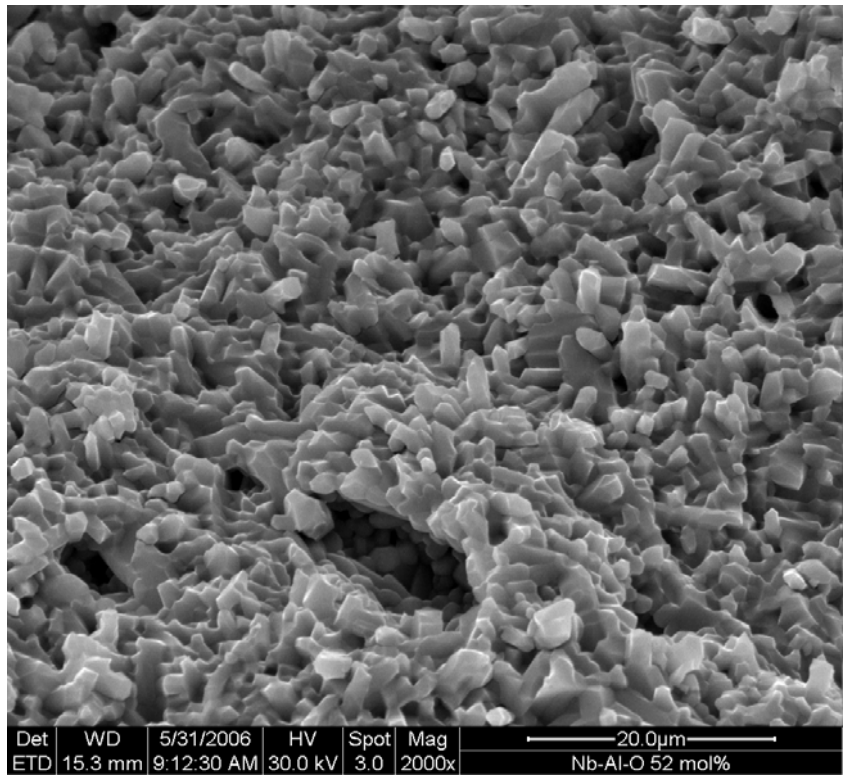
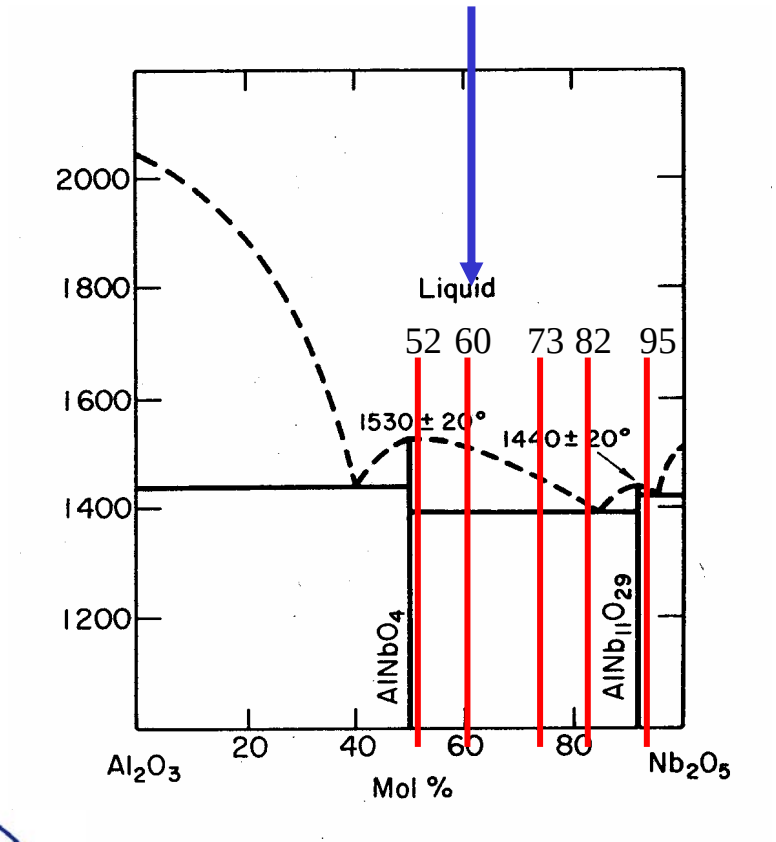
52 mol % Specimen – Fracture Surfaces

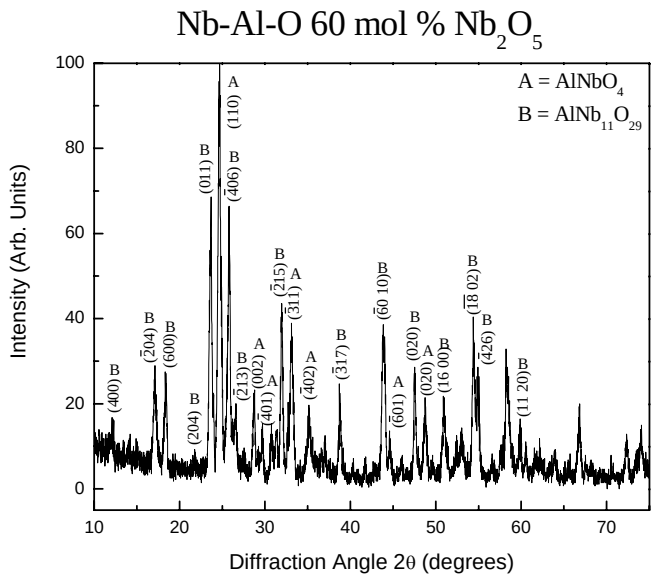


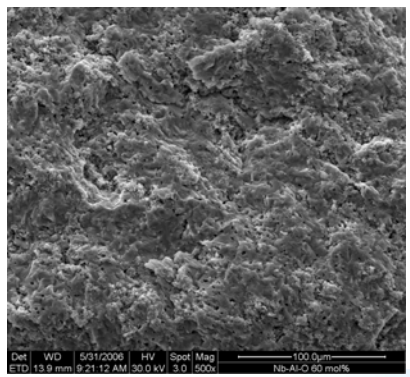


No glassy phase is visible

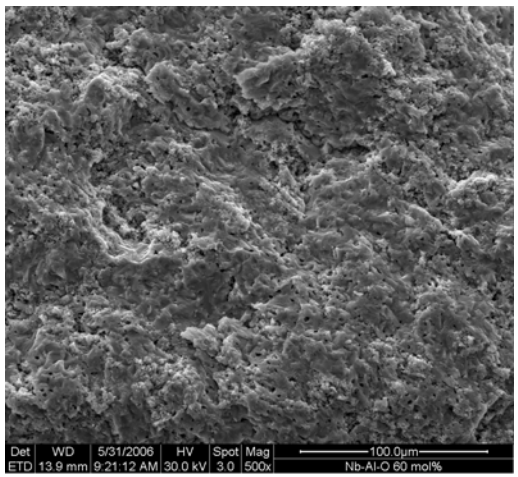
60 mol % Specimen

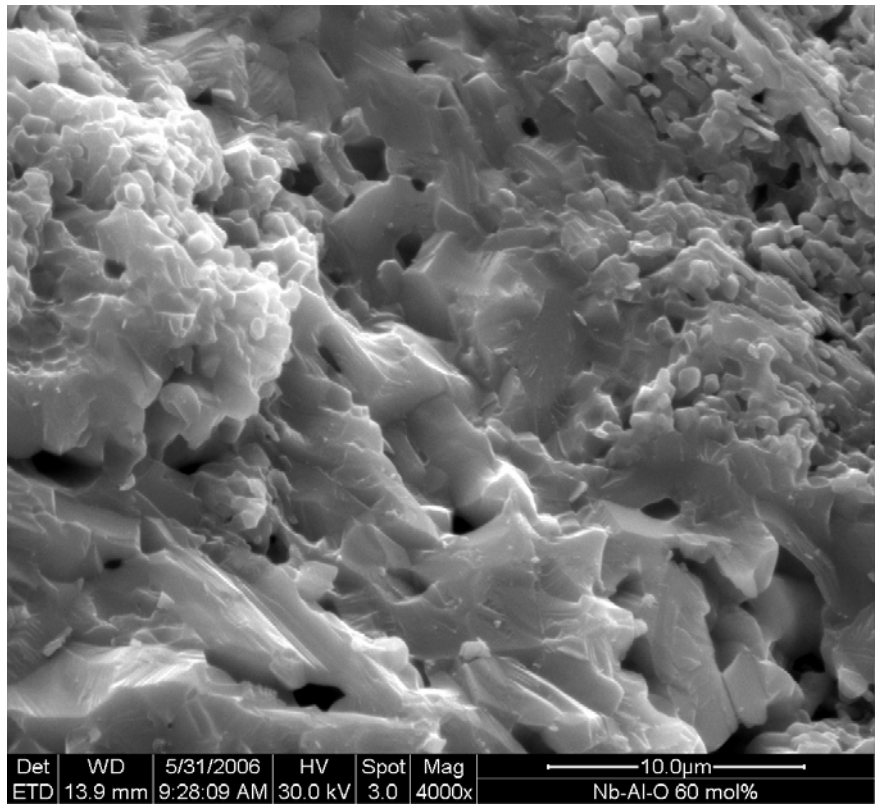






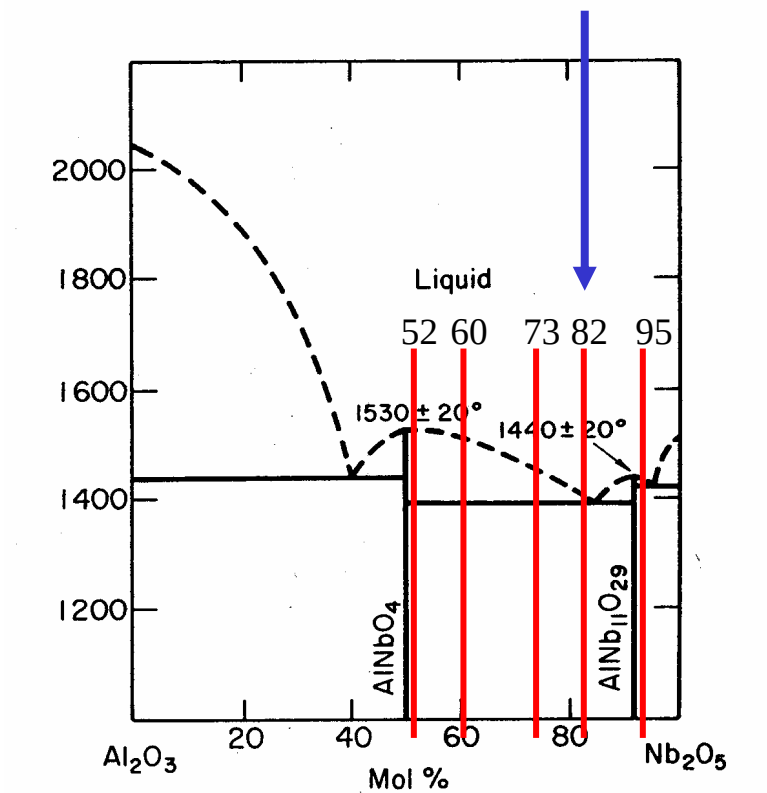
60 mol % Specimen – Fracture Surfaces



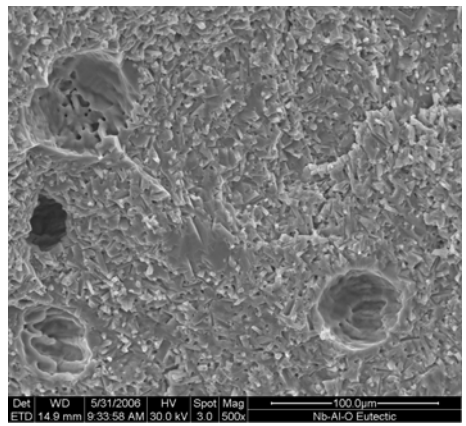


No glassy phase is visible

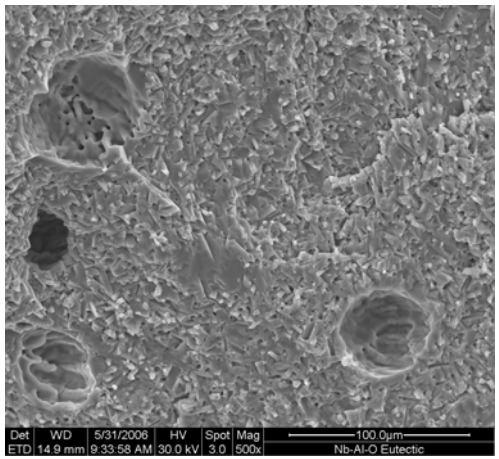
82 mol % Specimen (hot pressed)

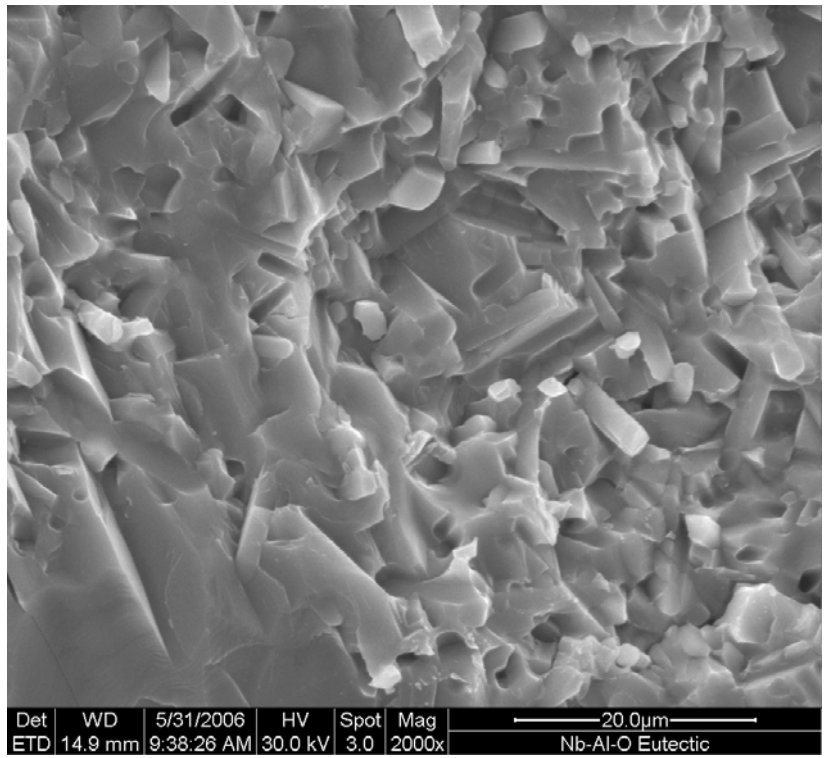


XRD: $AlNbO_4$ and $AlNb_{11}O_{29}$



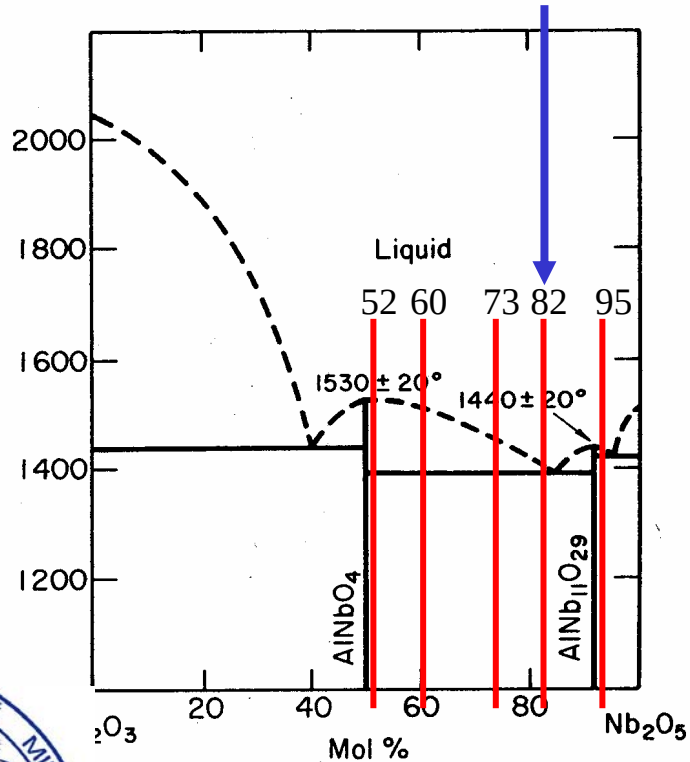
82 mol % Specimen – Fracture Surfaces





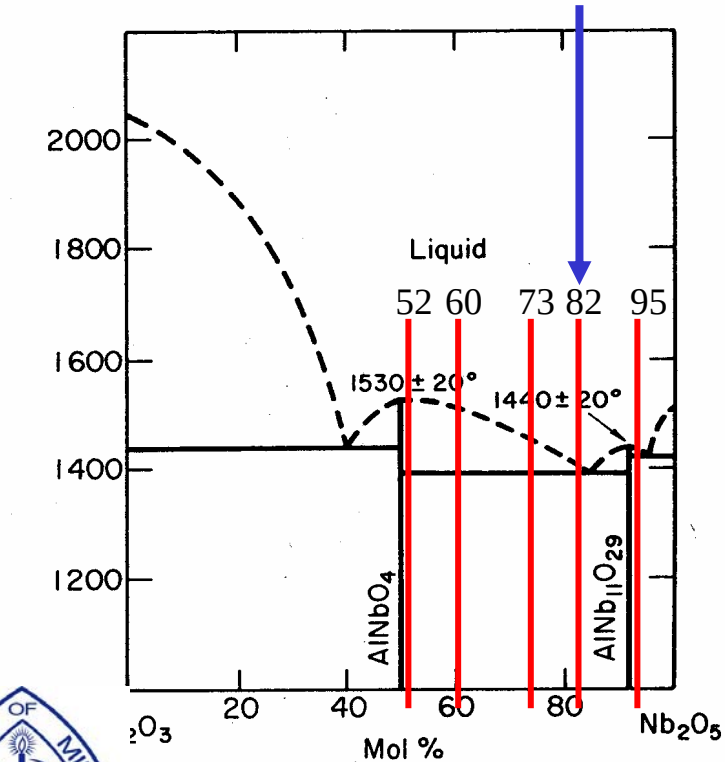
No glassy phase is visible; evidence for vapor phase sintering

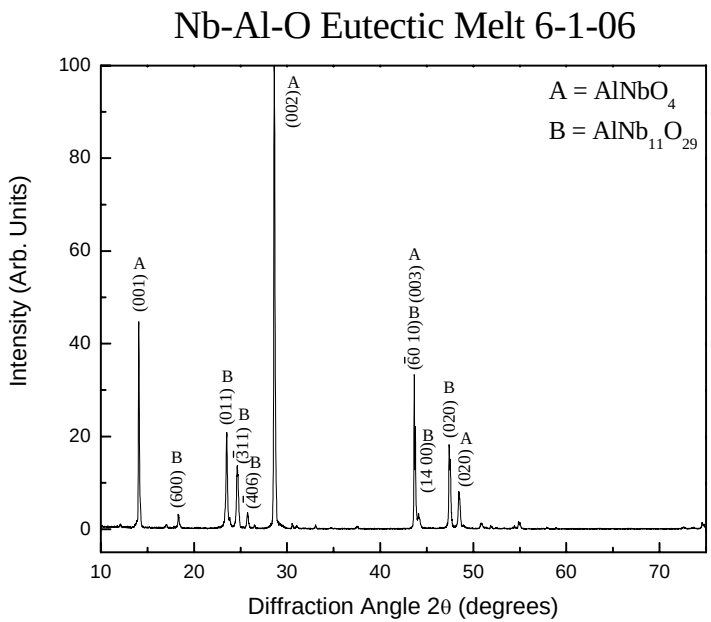
Heat Treatment Experiment: Re-Heat and Quick-Cool 82 mol% Specimen



- Heat to 1450°C in air
- Held for 5 minutes
- Turn off furnace (~100°C/min initial cooling rate)

Re-Heat and Quick-Cool 82 mol% Specimen





Note Texture

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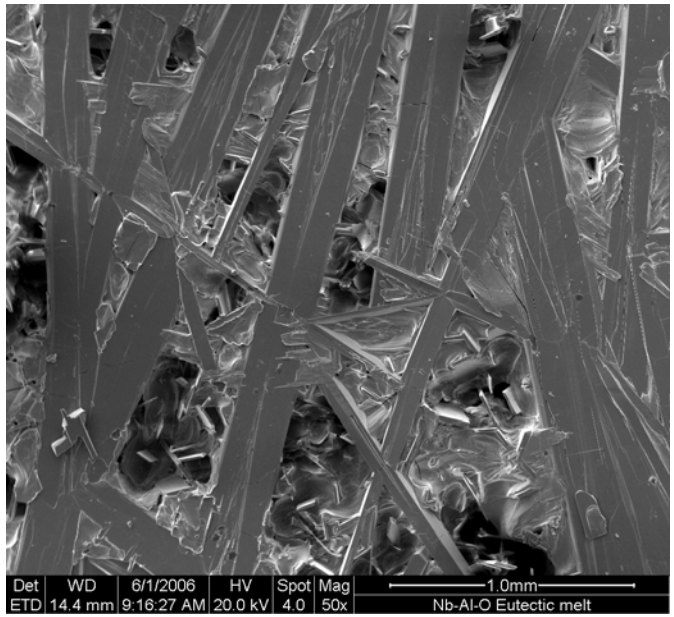
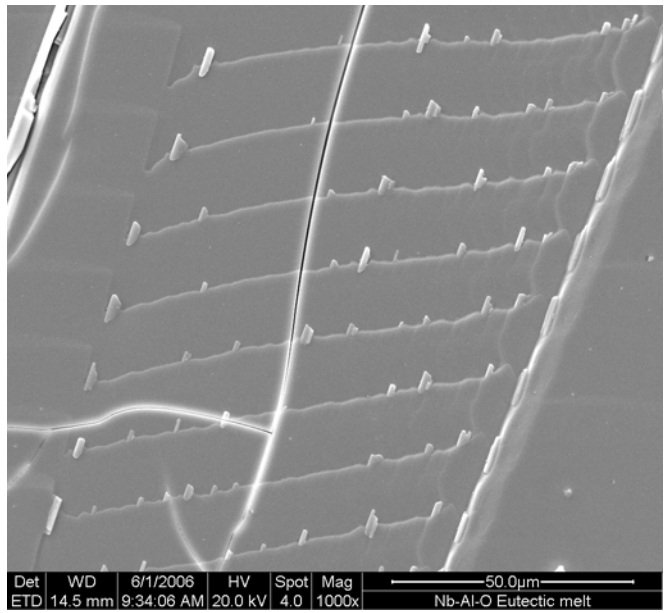
Re-Heat and Quick-Cool 82 mol% Specimen

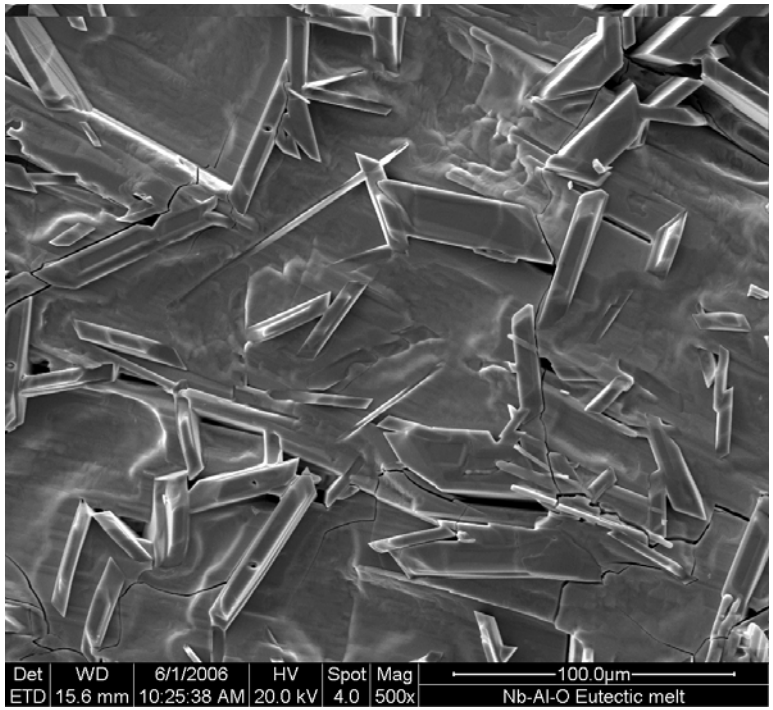


Note Texture – elongated needles

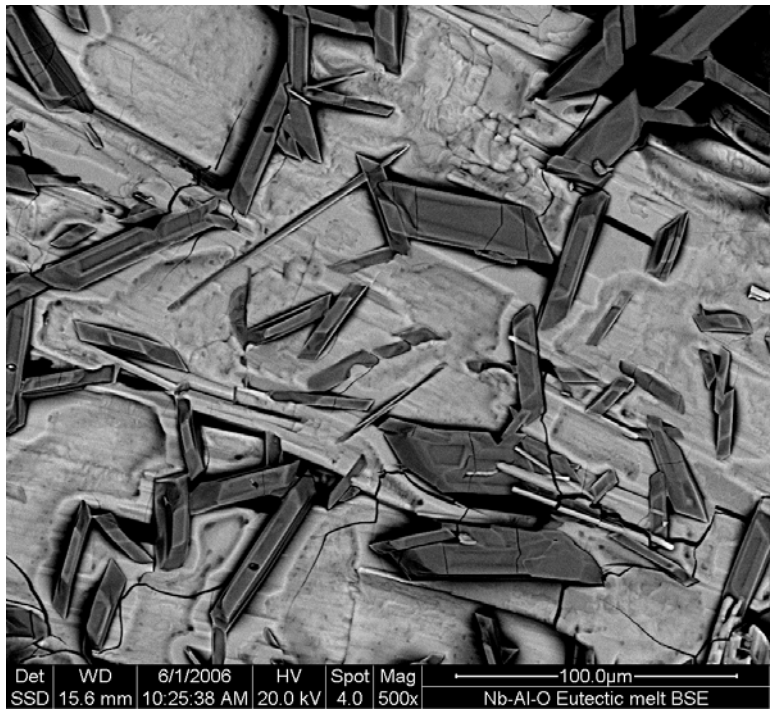


Evidence for vapor phase sintering

Re-Heat and Quick Cool 82 mol% Specimen



SE Image



BSE Image

Possible evidence for glassy phase

CTE of Niobium-Aluminum-Oxygen Compounds Close to Al_2O_3

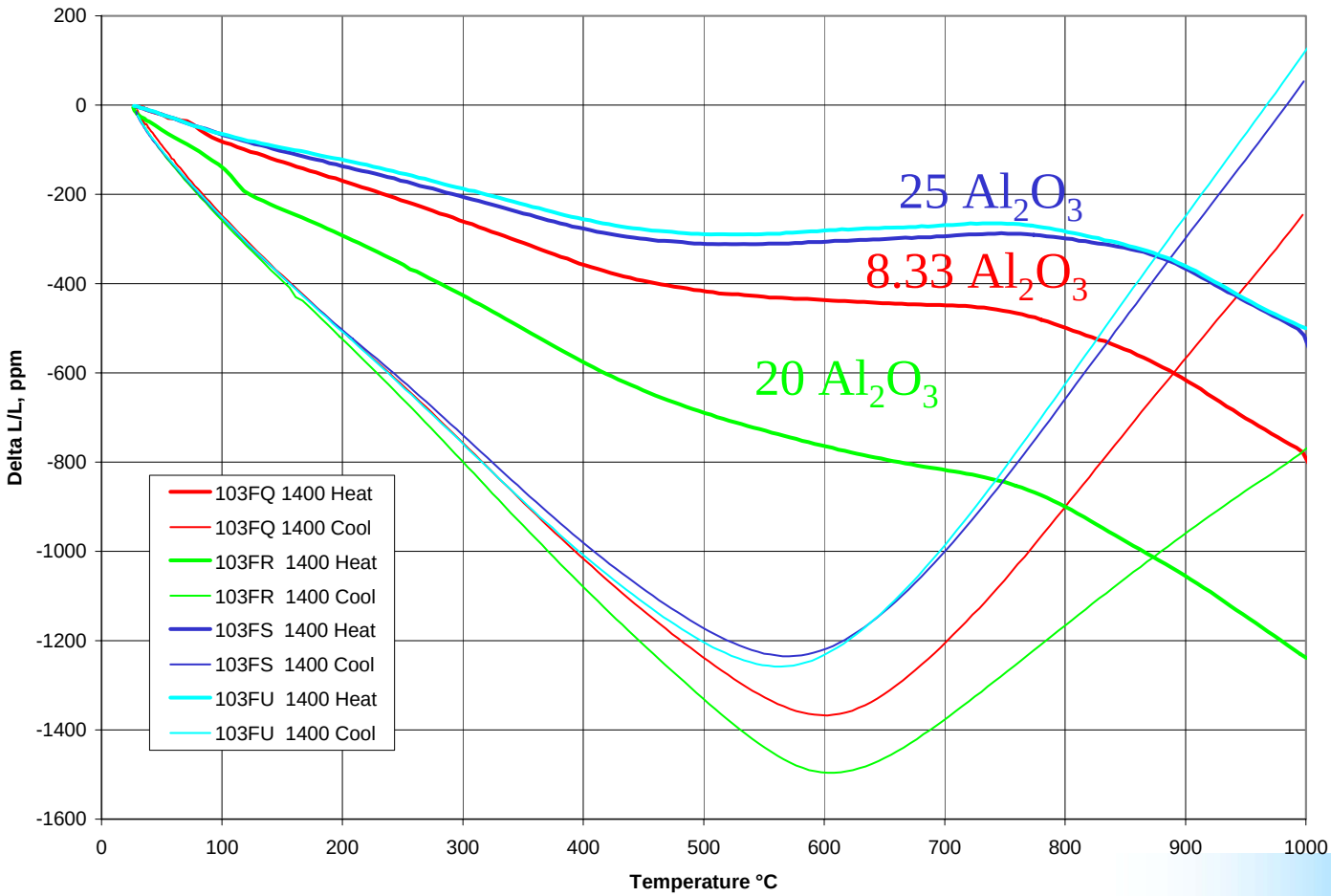


Figure from Matt Dejneka, Corning, Inc.

CTE of Niobium-Aluminum-Oxygen Compounds Close to Al_2O_3

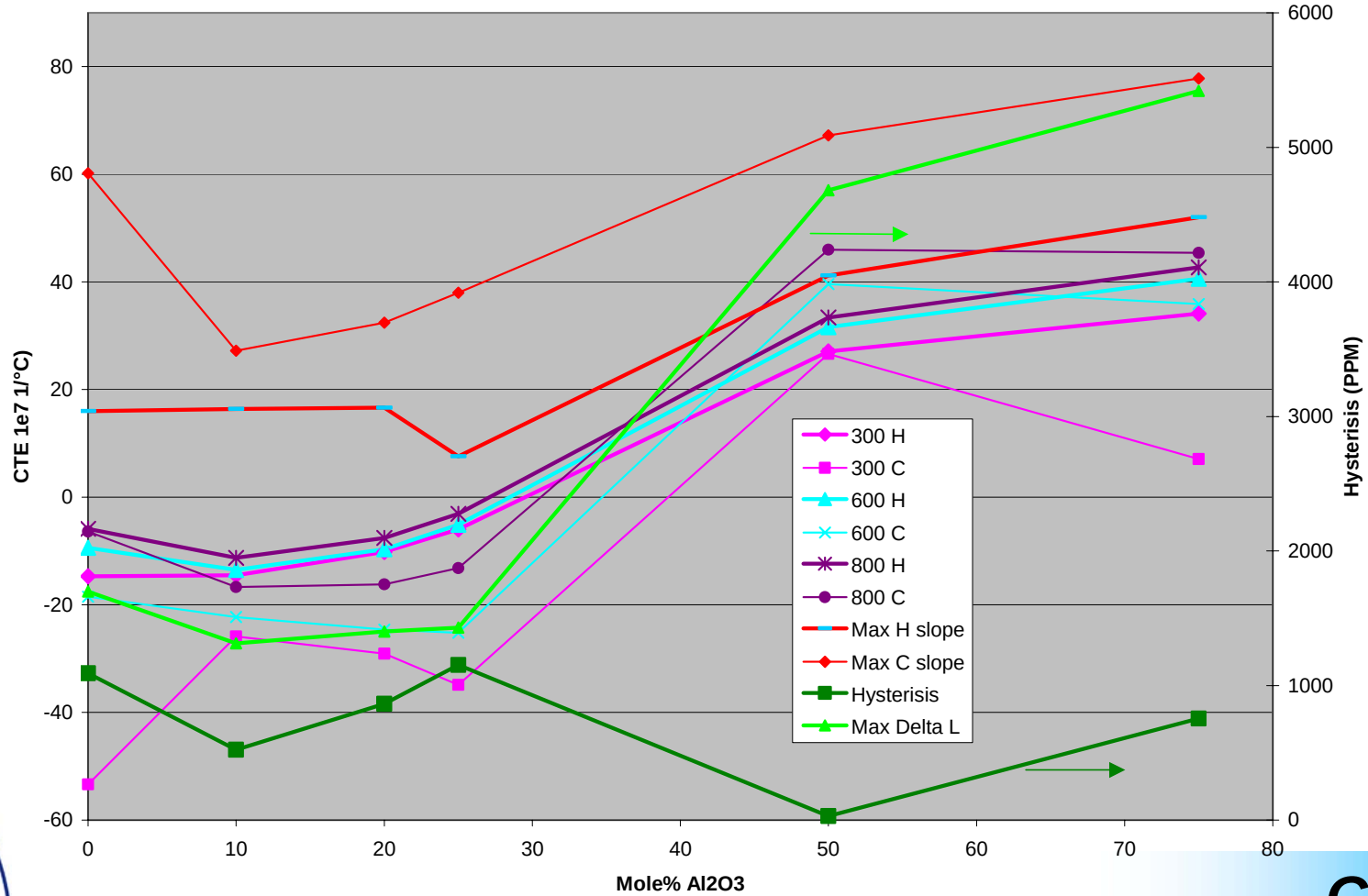


Figure from Matt Dejneka, Corning, Inc.

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Conclusion

- Tough-looking microstructures produced
  - CTE match with Al_2O_3 may be possible
- Glass formation conditions are elusive
- Future
  - Melt and quick-cool experiments (longer times in melt)
  - Form tough joints with eutectic composition

Colorado has the foundation for developing business clusters around SOFC technology

Academics
- Universities -- engineering, business, cutting-edge research
- Community colleges -- knowledgeable work force

Local and state government
- Colorado Fuel Cell Center

National Renewable Energy Laboratory
- Renewable energy, energy efficiency, distributed generation

Fuel cell systems development and manufacturing
- Versa Power Systems (Golden)
- Mesoscopic Devices (Broomfield)
- ITN Energy Systems (Littleton)

Balance of plant components
- TDA Research (Wheat Ridge)
- Vairex (Boulder)

Ceramics industrial base
- CoorsTek