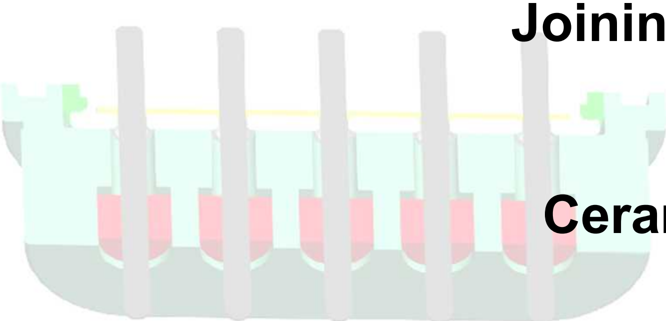
SAND2008-2960C

Effects of Glass-Ceramic Sealing Cycle on Paliney-7 Pin Microstructure and Hardness

(Paliney is a trade name of Deringer-Ney Inc., Bloomfield, CT)



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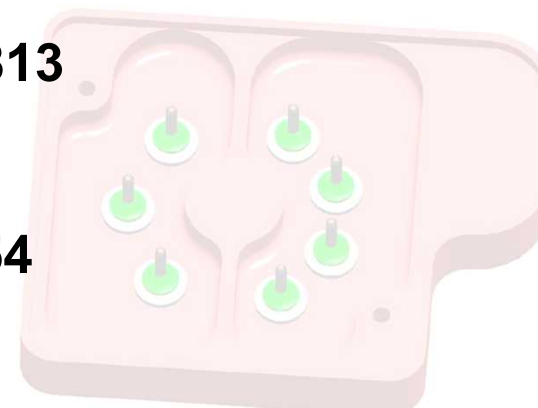

JOWOG-28 Meeting
May 5th, 2008

National Nuclear Security Administration

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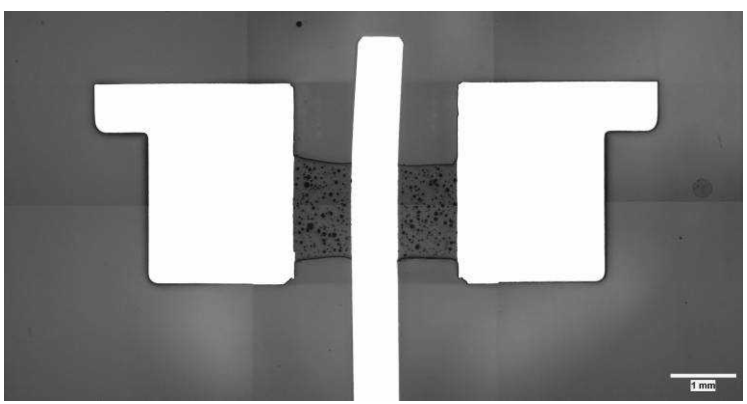
Motivation

- **Initial glass-ceramic/metal sealing trials resulted in Paliney-7 pin hardness that was marginal or low. The requirement is >300 HKN (100g Knoop microhardness). The initial seal cycle consisted of slow-cool (6˚C/min) from 1000˚C to 660˚C, followed by faster cooling (25˚C/min) to 482˚C where the pins are age hardened in-situ.**

- **In addition, differences among Pal-7 heats were observed with one particular “wire” lot showing significantly lower hardness.**



“single-pin” G-C/metal seal with Pal-7 pin and 304L shell

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Paliney-7 Precious Metal Contact Alloy

- Pd-based alloy with the following composition (ASTM B540):

Element	Composition, weight %
Palladium	34.0–36.0
Silver	29.0–31.0
Copper	13.5–14.5
Gold	9.5–10.5
Platinum	9.5–10.5
Zinc	0.8–1.2
Total platinum group metal impurities (iridium, osmium, rhodium, ruthenium)	0.1 max
Total base metal impurities	0.2 max

- Melting point (solidus) is 1015˚C, so we must be careful with regard to furnace overheating, etc. Our latest process is to lower the G-C/Metal sealing temp. from 1000˚C to 975˚C.
- The standard age hardening (precipitation hardening) treatment is 482˚C for 45 minutes. According to ASTM B540, Knoop hardness in the annealed condition is 200-260HKN (UTS~105-130ksi) and in the hardened condition it is 310-360HKN (UTS~155-185ksi).

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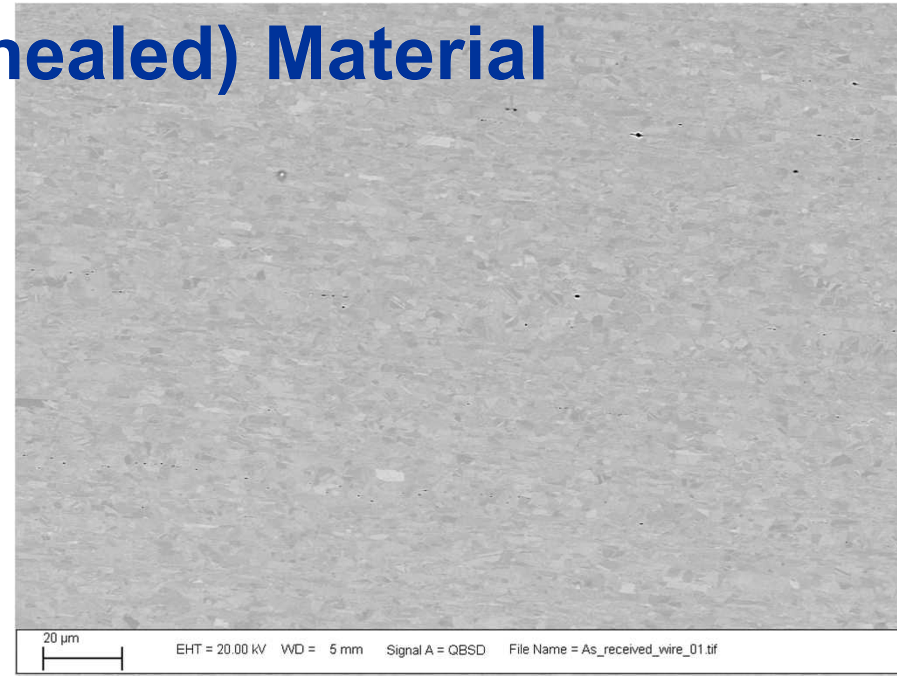
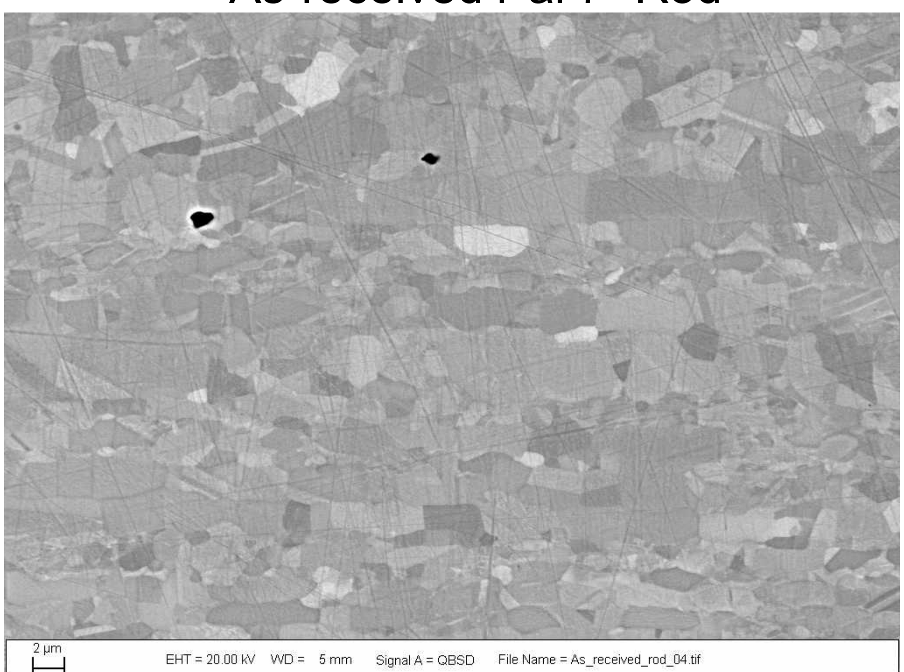
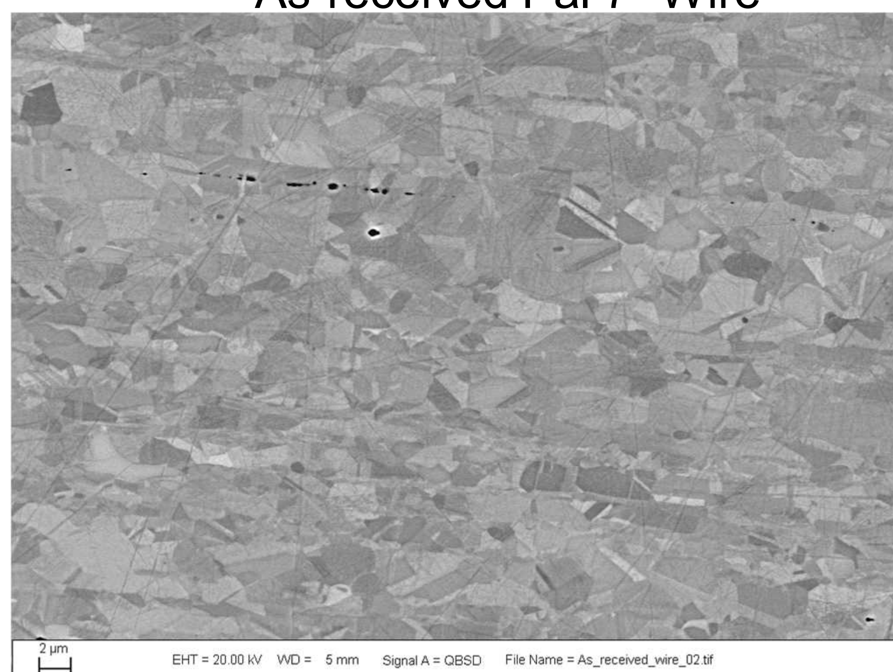
As-Received (Annealed) Material

As-received Pal 7 “Rod”



As-received Pal 7 “Wire”





As-Received (Annealed) Material

• Some differences observed in Knoop hardness of as-received, annealed material:

As-received Pal-7 rod: 193 Knoop (UTS=106ksi reported by manufacturer)

As-received Pal-7 wire: 226 Knoop (UTS=116ksi reported by manufacturer)

• In the as-received condition, Pal-7 rod has slightly larger grain size than Pal-7 wire (and a more “duplex” grain structure). The wire has slightly smaller grain size and possibly a more deformed grain structure. These differences account for the lower hardness observed in as-received Pal-7 rod compared to wire.

Two heats of Paliney-7 displayed different hardness responses to BPS glass-ceramic processing: "Rod" heat was marginal, "Wire" heat had low hardness

Results from early G-C/metal seal trials

Thermal Profile	Paliney 7 Pin Hardness (Knoop Hardness)
RT to 1000C @ 25C/min; hold 12min; to 660C @ 6C/min; 0min hold; to 482C @ 25C/min with 45 min hold; to RT @ 5 C/min	Rod 293 / 307
RT to 1000C @ 25C/min; hold 12min; to 660C @ 6C/min; 0min hold; to 482C @ 25C/min with 45 min hold; to RT @ 5 C/min	Rod 298 / 302
RT to 1000C @ 25C/min; hold 12min; to 660C @ 6C/min; 0min hold; to 482C @ 25C/min with 45 min hold; to RT @ 5 C/min	Wire 259

Chemical analysis results from two heats of Pal-7

Melt #	Composition (wt.%)							
	Ag	**Zn**	**Pd**	**Cu**	**Ni**	**Au**	**Fe**	**Pt**
W34680W (wire)	30.39	0.97	34.82	14.09	0.02	10.00	0.01	9.84
W43004W (rod)	30.07	0.94	34.86	13.88	<.0014	9.98	<.0024	9.83

- **Only slight differences in the bulk chemistry of the heats**
- **"Rod" vs. "wire": processed the same except that rod is "batch annealed" (short lengths are heat treated in a batch oven) and wire is "strand annealed" (continuous feedthrough of wire through an oven)**
- **Glass sealing process at 1000˚C *should* remove any effects of prior processing of the materials**
- **However, minor differences in chemistry, not shown in the melt cert., could affect the precipitation hardening process and the final hardness after G-C sealing**

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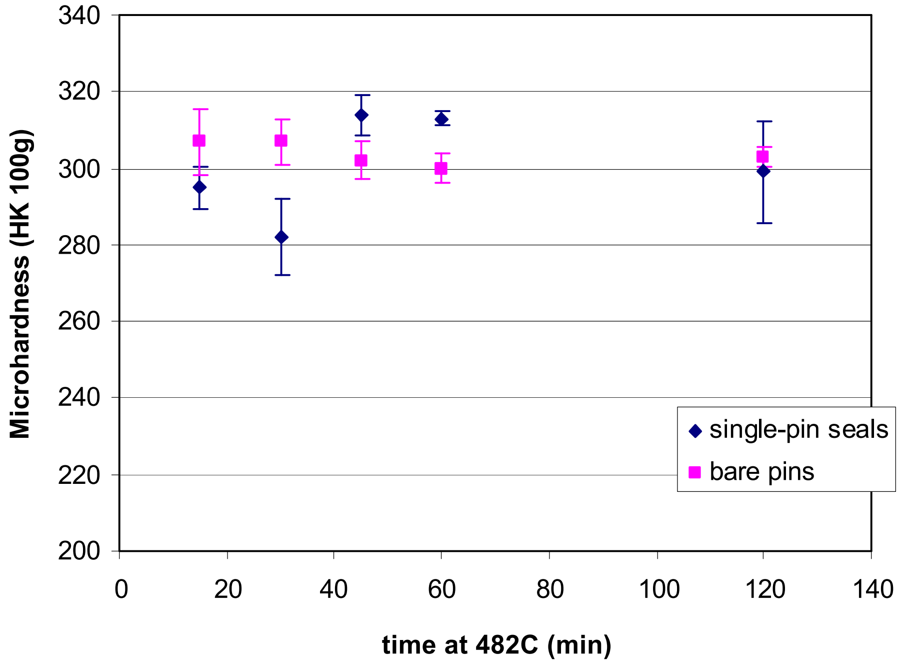
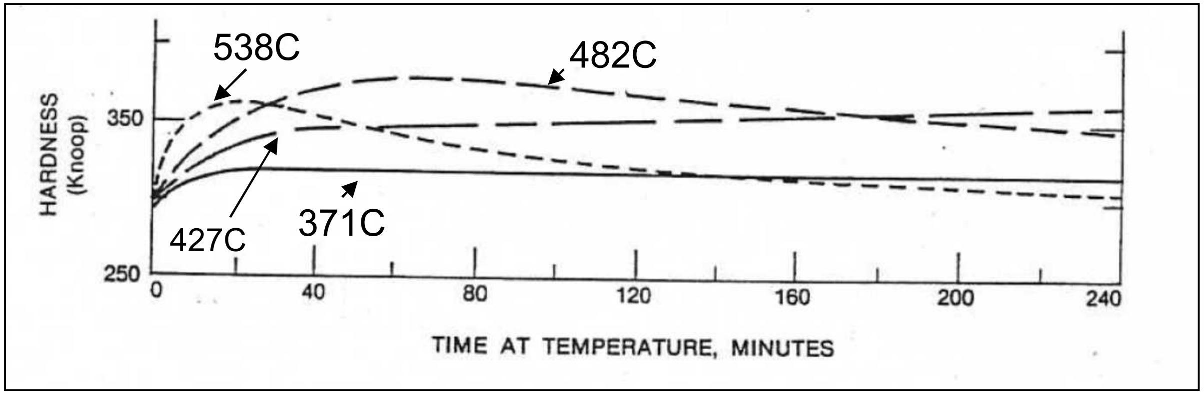
1st Attempt to Improve Pin hardness –
Aging Time at 482˚C – showed no significant effect on final hardness



- Varied the hold time at 482˚C *after* cooldown from G-C/metal sealing
- Hardness values were low or marginal in all cases ("wire" heat)
- No consistent trend of hardness vs. age hardening time



S. Brooks and G. Reed, "Age Hardening Ney Alloys", *Ney Scope*, Vol. 22, No. 1, Jan. 1980.

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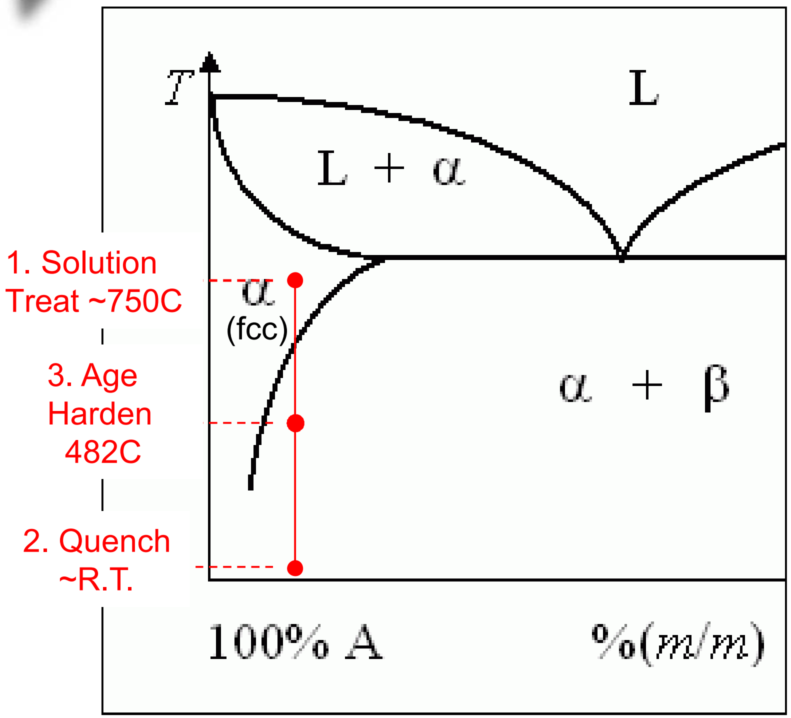
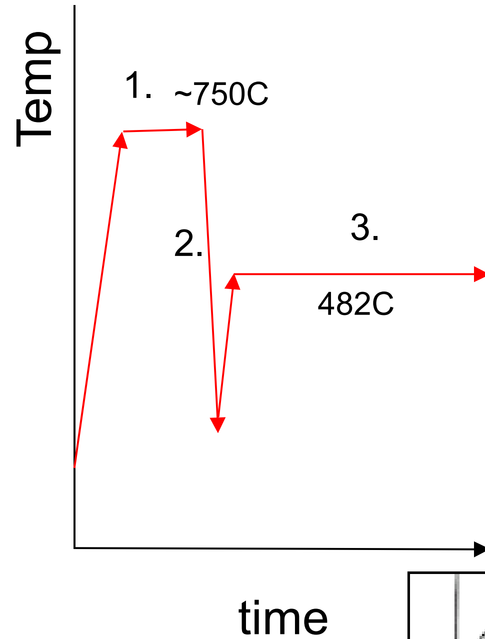
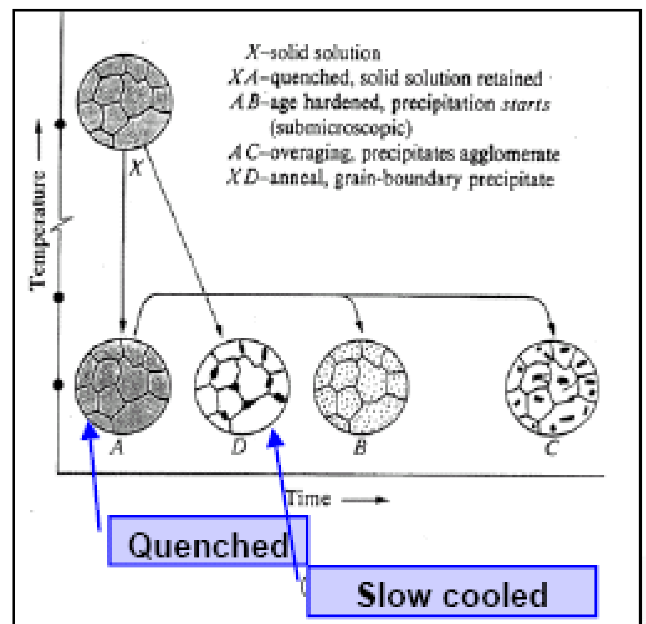
Typical Age-Hardening Process for Paliney-7:

Solution treat ~750-850˚C, fast quench, age at 482˚C





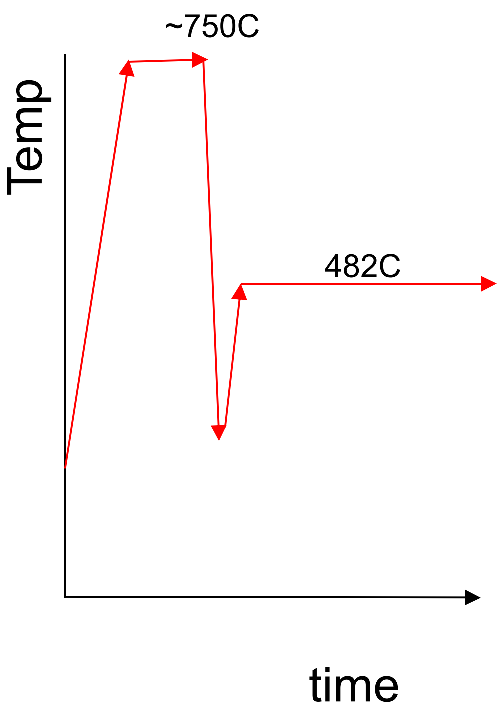
- Typical solution treat temp. is 750˚C or above, according to the vendor Deringer-Ney

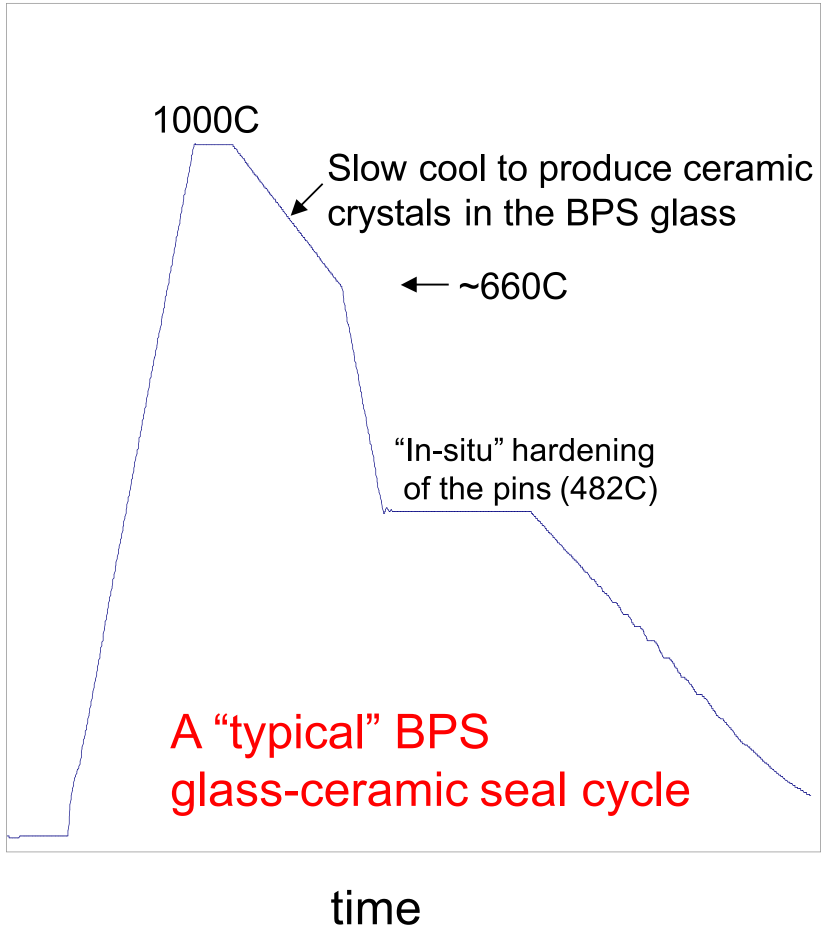


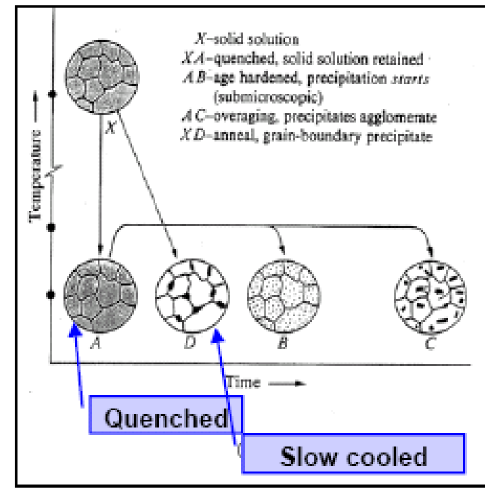
- Binary phase diagram is used to illustrate age hardening…Paliney 7 is a much more complex multicomponent alloy
- It appears that the solvus for the age hardening precipitate is below approx. 700-725˚C
- The standard age hardening heat treatment of Paliney-7 is capable of producing 340-380 HKN

Compare to BPS glass-ceramic sealing cycle:
Slow-cooling through the apparent solvus range

Ideal precipitation-hardening process







- The slow-cooling rate and long time spent at high temperatures are the likely causes of reduced hardness

(Original thermal profile was slow-cool to 660C, then faster cool to 482C)

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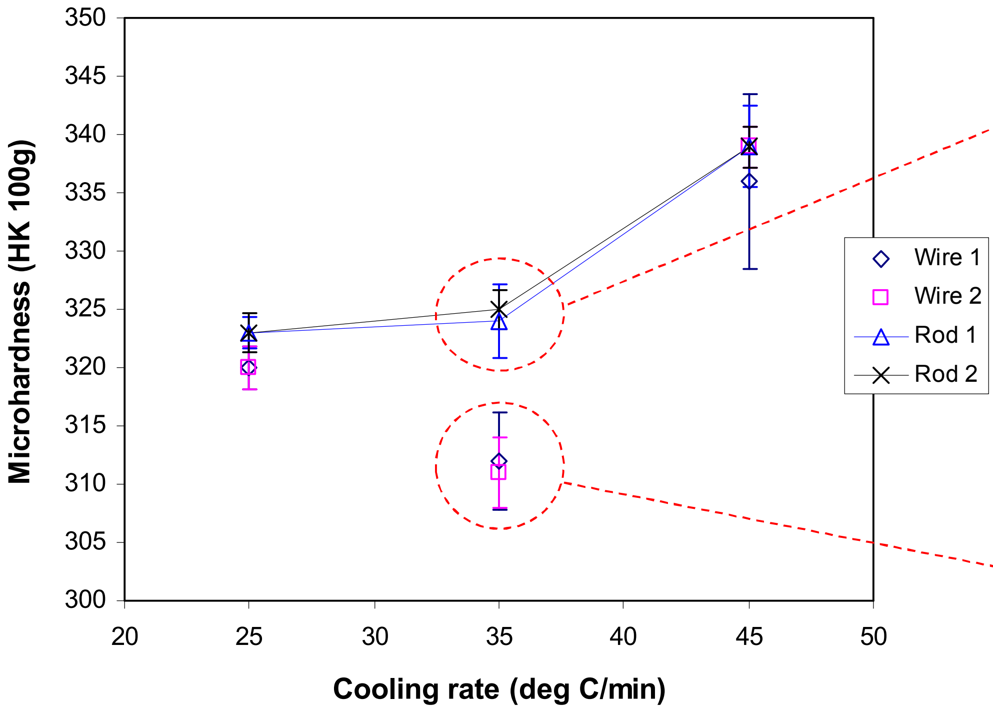
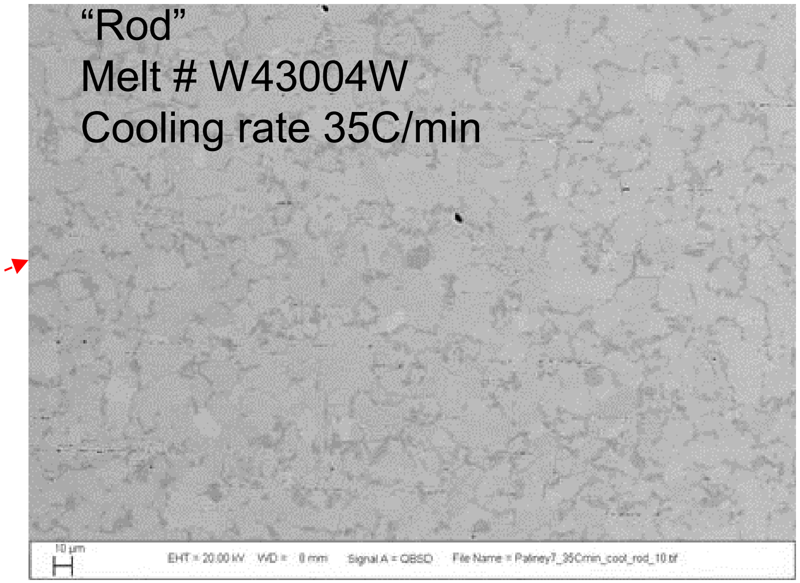
2nd Attempt: Cooling Rate Study -- Some Hardness and *Microstructural* Differences Between Rod and Wire Heats

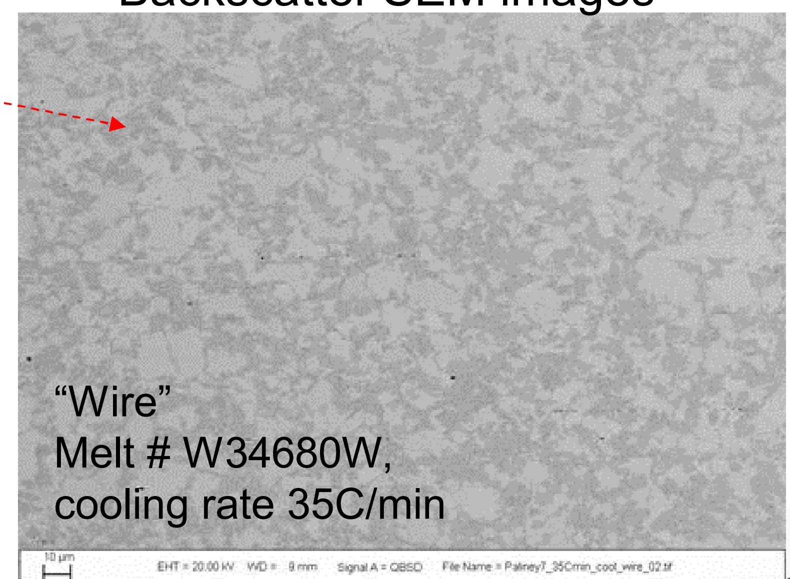
- Paliney-7 pin samples heated to 1000˚C and cooled at 25, 35, and 45˚C/min

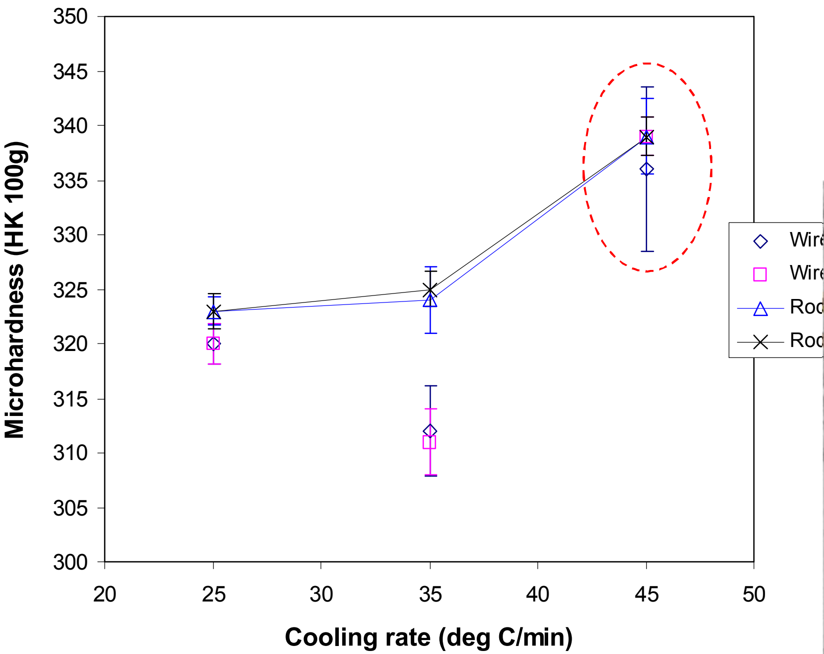


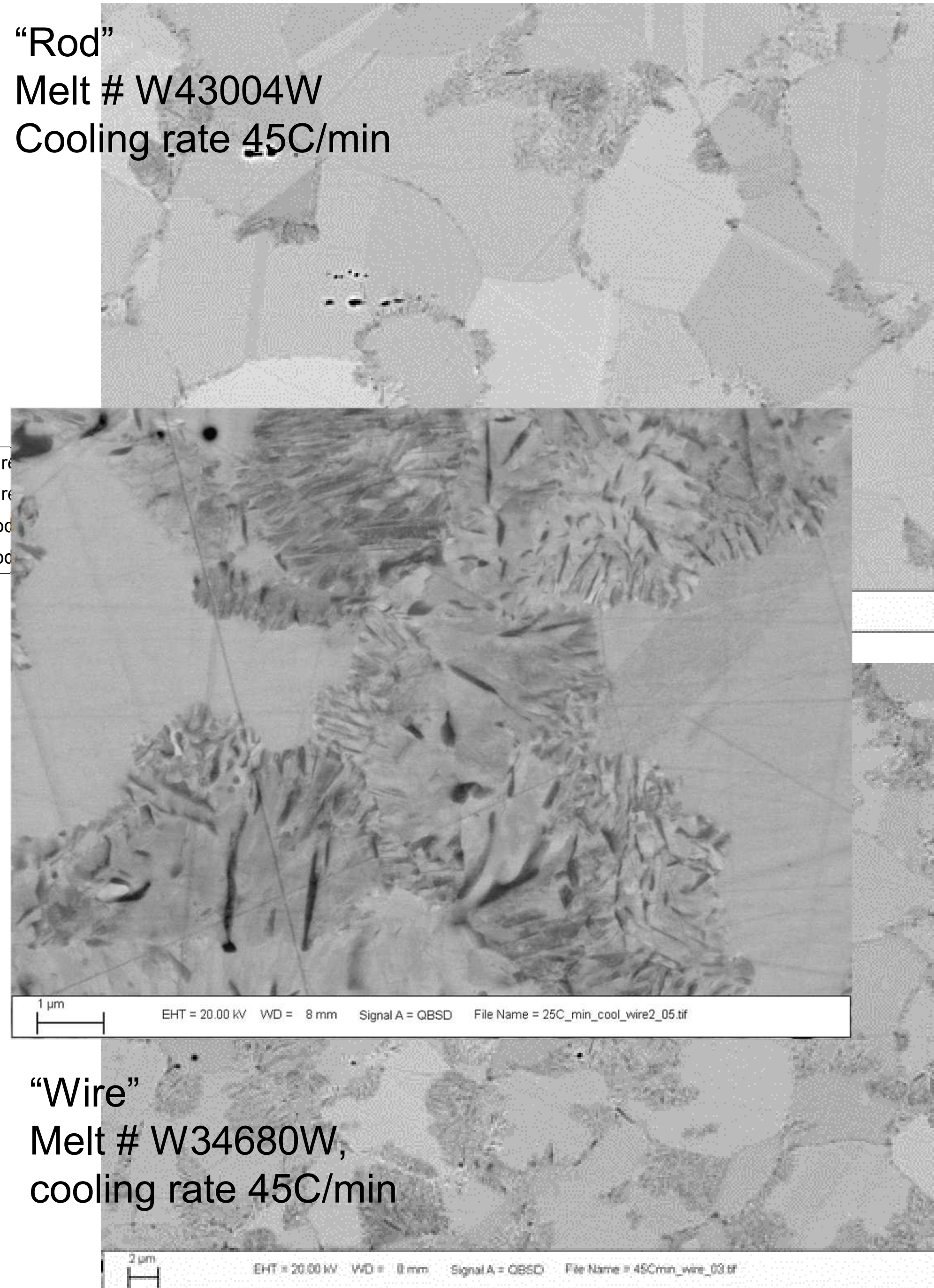
- **Some differences observed between rod and wire, although inconsistent with cooling rate.**
- **Backscatter SEM revealed *multiphase* Pal 7 microstructure.**



Backscatter SEM images





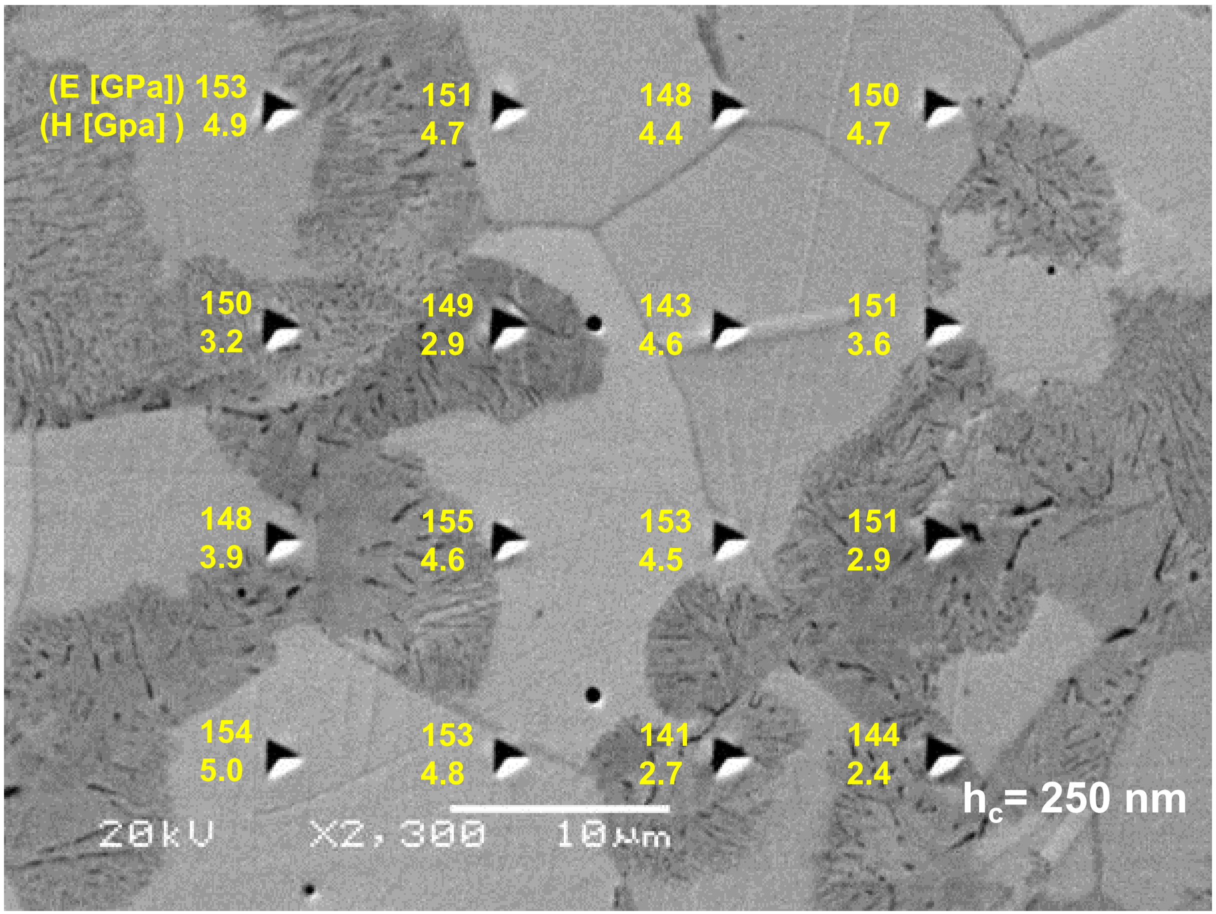


- **Multiphase Pal 7 structure found for other cooling rates as well.**
- **Lower amount of 2-phase regions along grain boundaries in the rod material.**
- **This suggested that lower hardness in wire is due to the 2 phase structure produced during G-C/metal seal processing.**

Nano-Indentation Results:

Dark 2-phase Regions are Softer than the Matrix Grains

- **Indent array covers different microstructural regions of the sample**



"Wire"
Melt # W34680W,
cooling rate 35˚C/min

E_{avg}= 150 ± 4 GPa
E (as per ASTM B540)= 117 GPa
•Discrepancy possibly due to indent 'pile-up'

H_{light}= 4.5 ± 0.4 GPa
H_{dark}= 2.8 ± 0.2 GPa

Bulk H (ASTM B540)= 3.2-3.9 GPa

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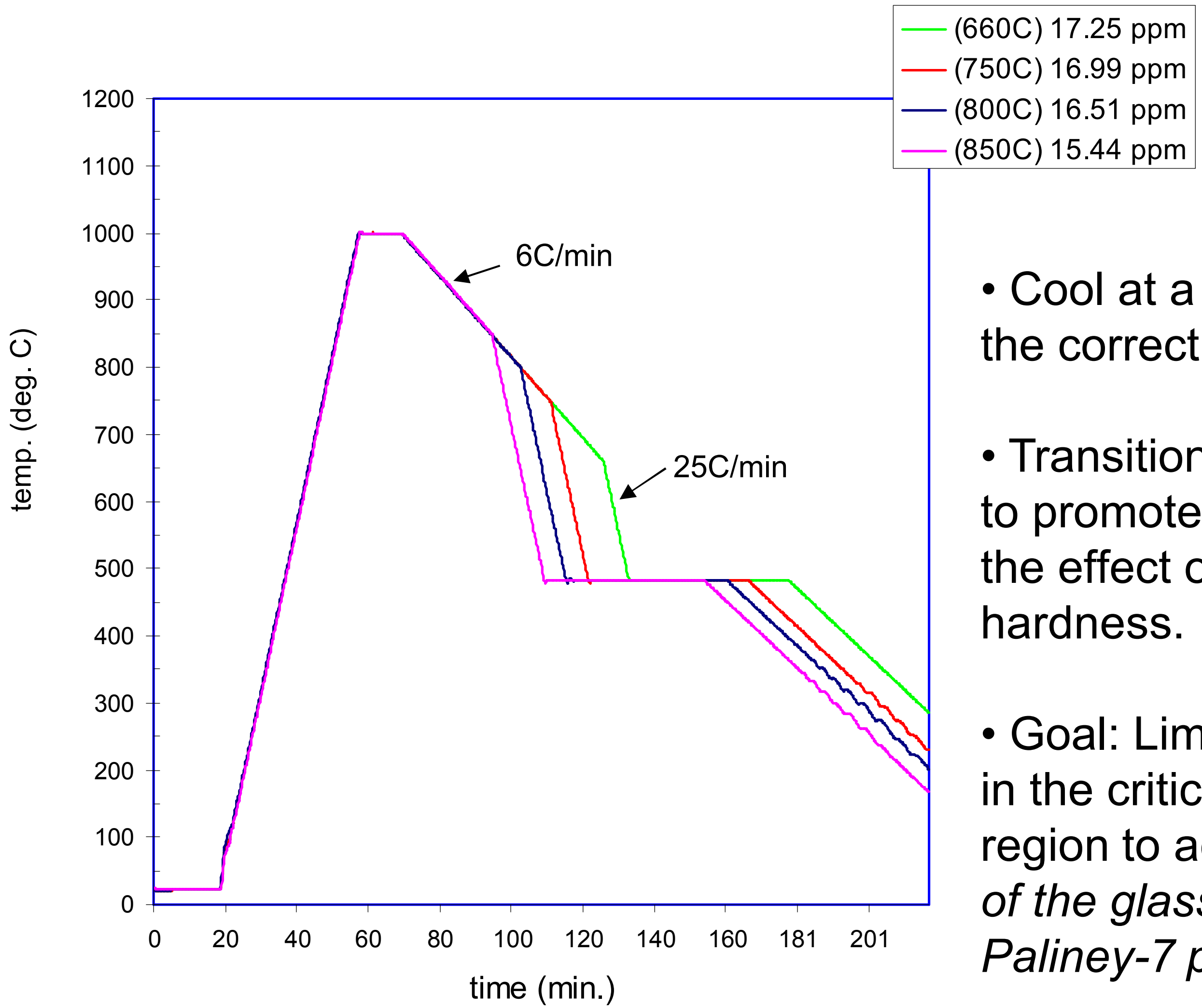
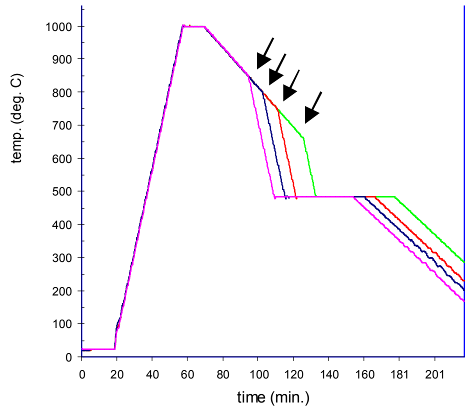
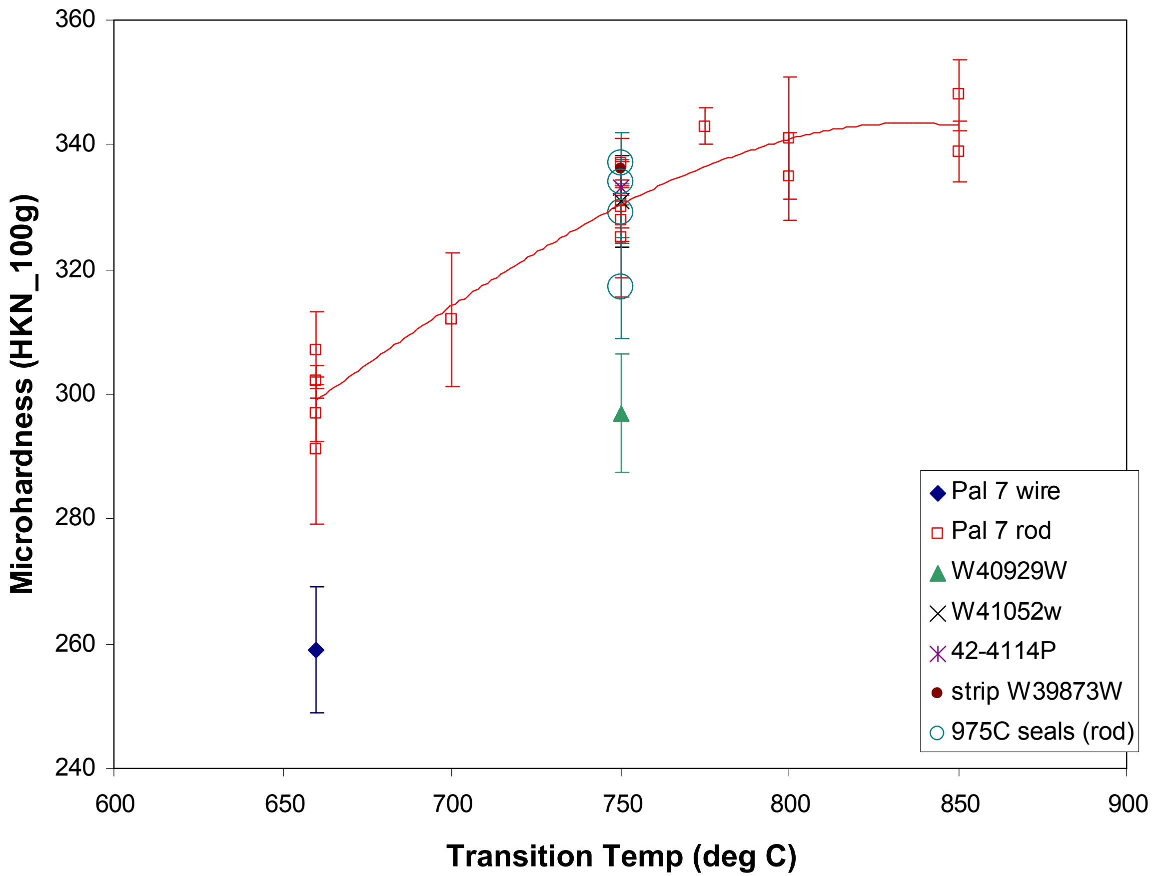
3rd (and final) attempt to understand and improve Pal-7 hardness:
Cooling-Rate "Transition" Study



- Cool at a slow rate initially to achieved the correct CTE of the glass-ceramic
- Transition to a faster cooling rate to promote pin hardening, analyze the effect of this transition temp. on pin hardness.
- Goal: Limit the amount of time spent in the critical Pal-7 precipitation region to achieve *both the desired CTE of the glass-ceramic and high Paliney-7 pin hardness.*

Positive Results: Consistent Trend of Increasing Pin Hardness with Increasing "Cooling Rate Transition Temp."





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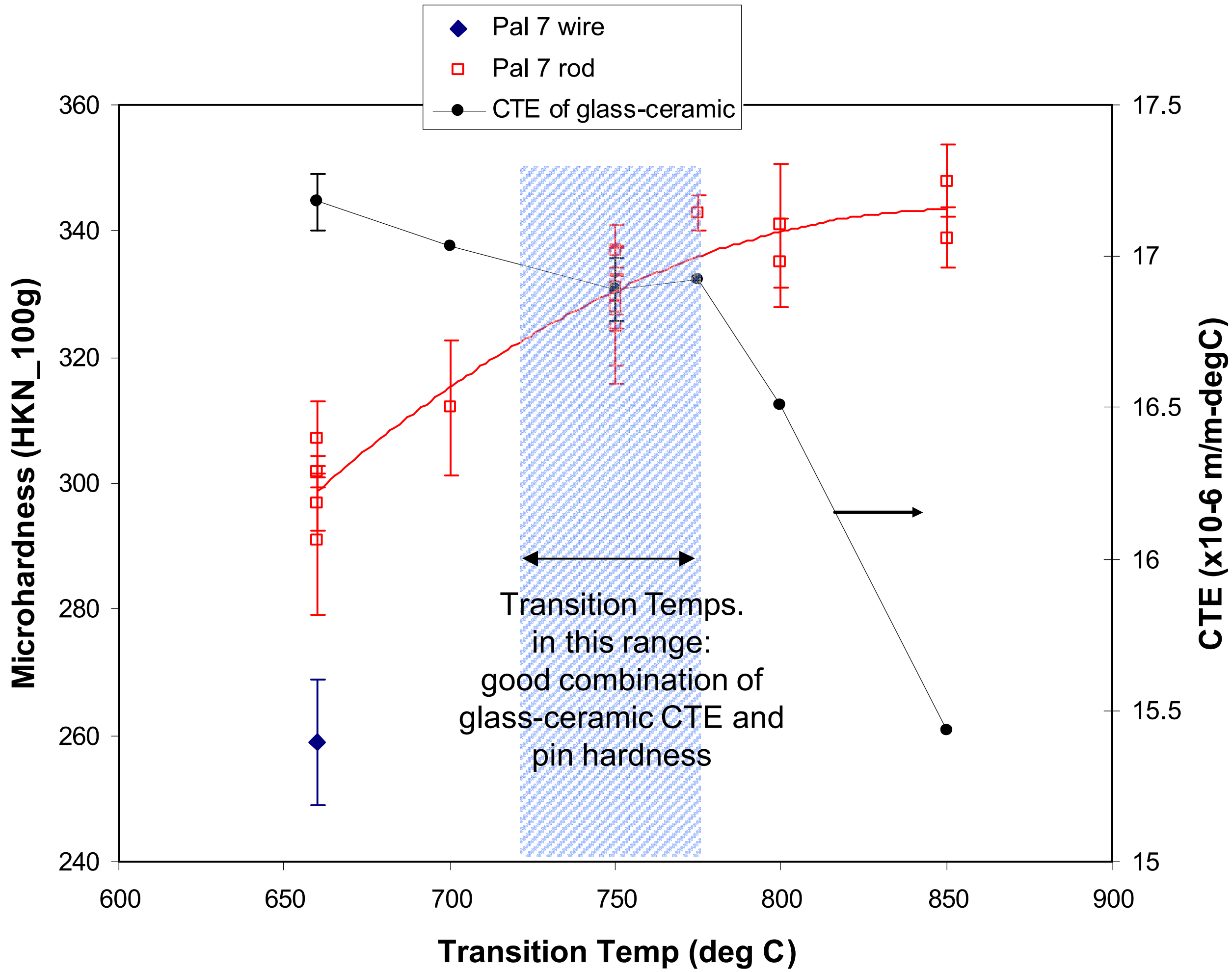
Combine with Glass-Ceramic CTE Data: A Processing Window has been developed for both Glass-Ceramic CTE *and* Pin Hardness



Superimposed CTE and Pin Hardness Results

What causes low hardness values?
Discontinuous Precipitation (DP)
(or discontinuous coarsening (DC)

- Precipitation of a 2-phase lamellar structure behind a moving grain boundary
- Coarse precipitate structure is generally detrimental to mechanical properties

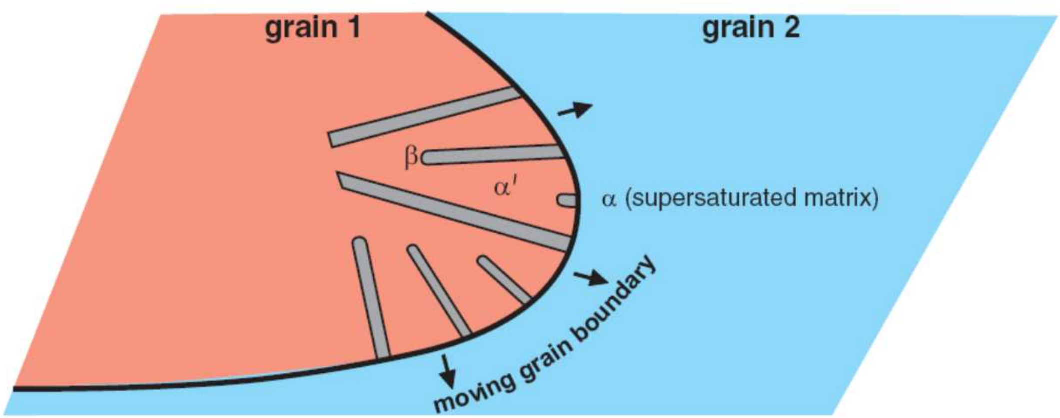
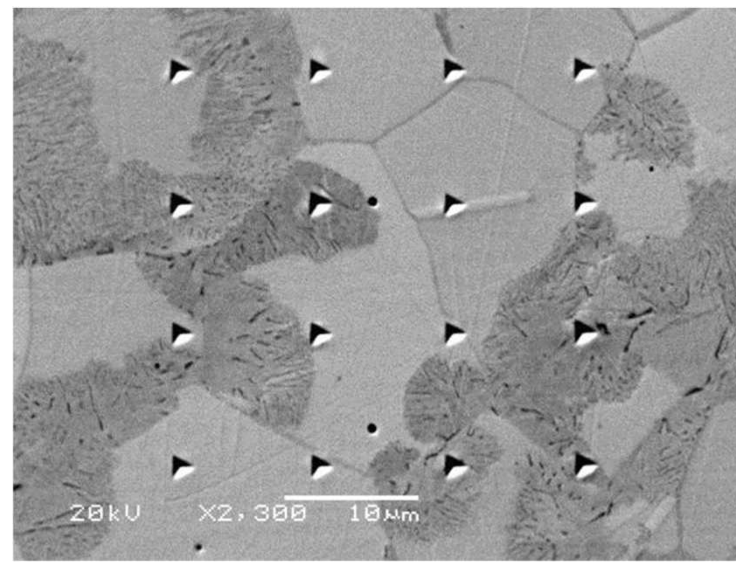


Fig. 1 Schematic of discontinuous precipitation, $\alpha \rightarrow \alpha' + \beta$



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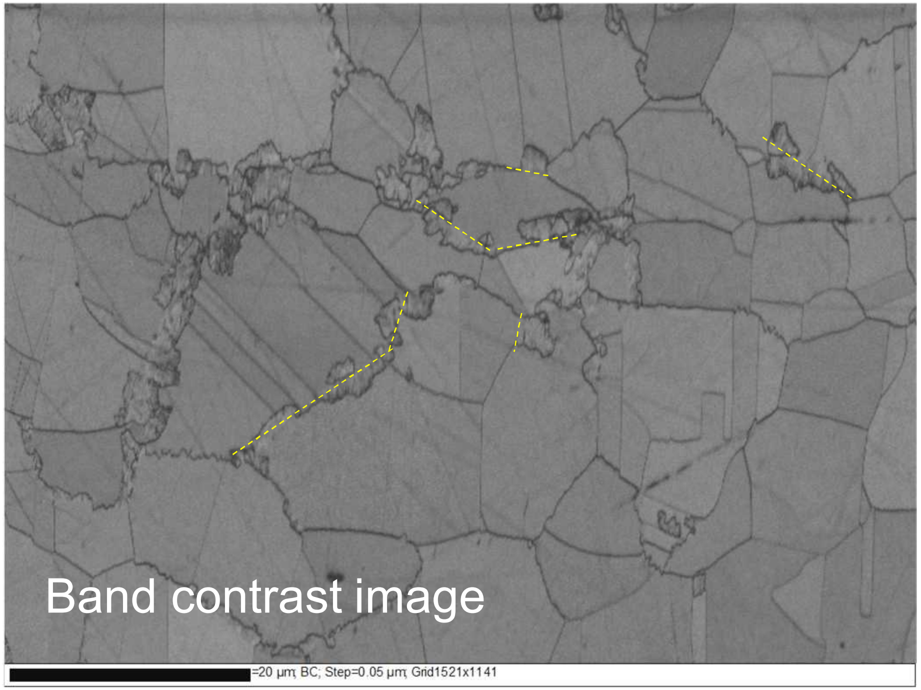
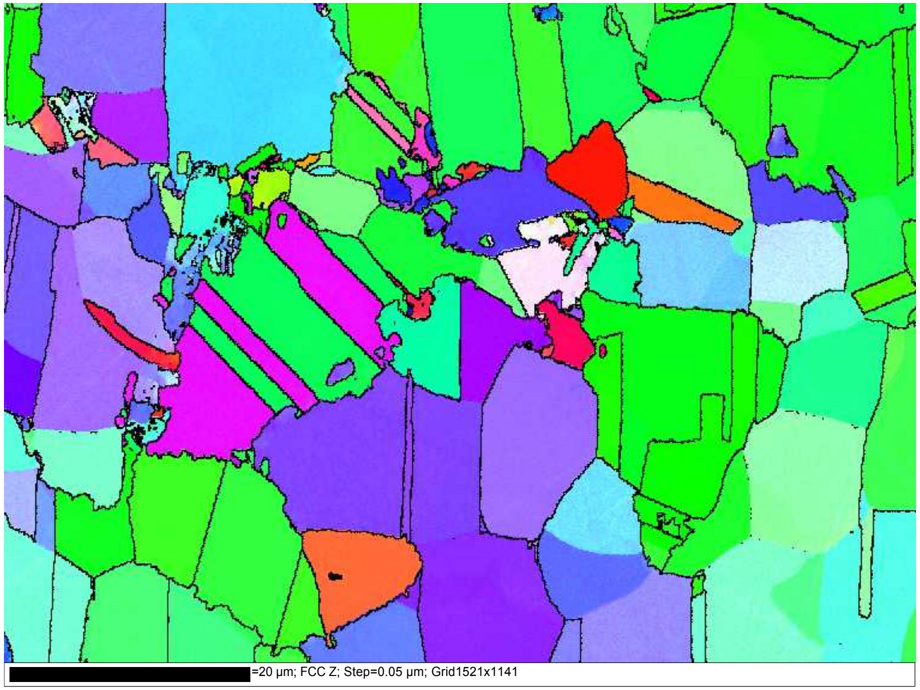
EBSD Characterization of Discontinuous Precipitation





EBSD orientation image of Pal-7 rod after cooling at 45C/min

EBSD shows that, in many regions, the fcc matrix of the lamellar two-phase structure has the same crystallographic orientation as the grain from which the reaction boundary had migrated. This is an essential characteristic of the discontinuous reaction.

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Summary

• Low hardness in Pal-7 was found to be due to discontinuous precipitation during the G-C/metal sealing process.

• Some heats of Pal-7 are more susceptible to DP and show lower hardness after G-C seal cycle. Reasons for heat-to-heat differences are unknown.

• Bottom Line: A processing window was found which gives both acceptable Pal-7 pin hardness *and* the correct glass-ceramic CTE. The important aspect is to change to a fast cooling rate as early as possible, thereby limiting the time in the detrimental DP temperature range.

Future Work

- Understand the metallurgy of Paliney-7 precipitation process. The results appear to support the DP range around 700-725˚C. If you slow-cool below this temp, there will be significant "discontinuous"/coarse precipitation and lower hardness.
- What is the precipitate phase in DC? Is it different than the normal strengthening ppt.?
- What is the trade-off among precipitate vol. %, matrix grain size, and 2-phase region hardness (lamellar spacing)?

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Acknowledgements

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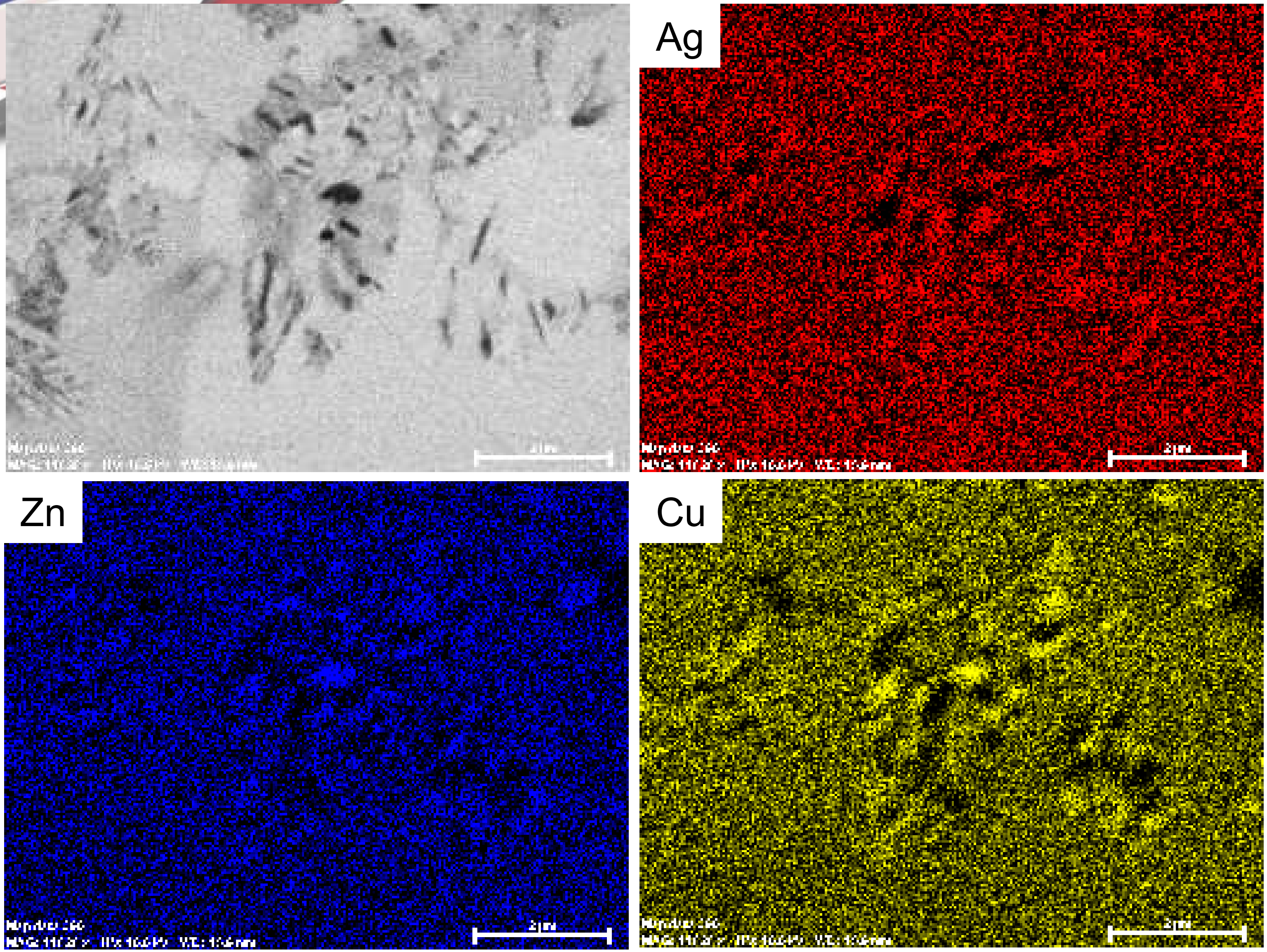

EDS maps.
Possibly higher Ag, Cu, and Zn in the dark precipitates. Difficult to tell conclusively.
TEM samples needed.