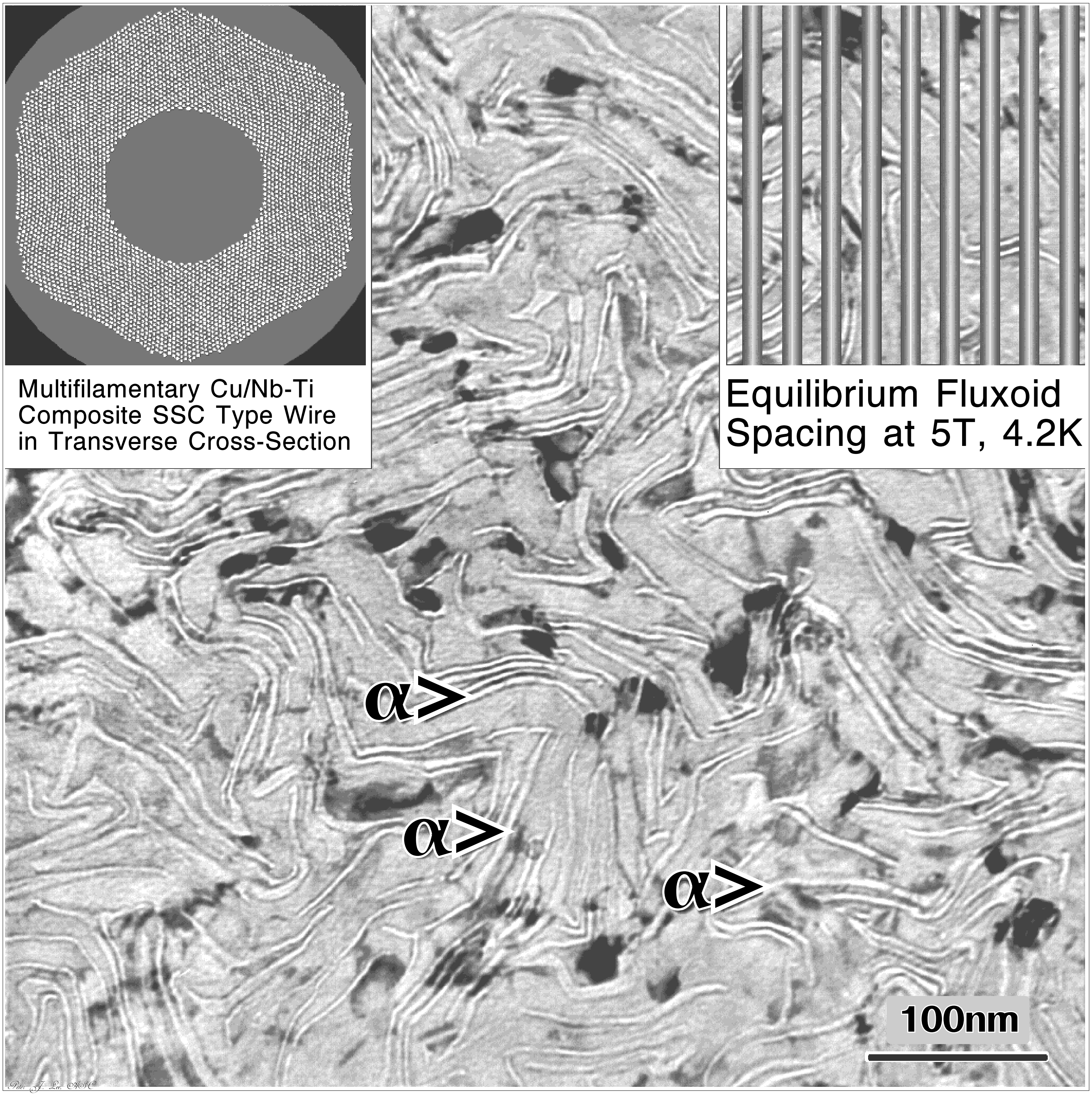
University of WI-Madison,
Applied Superconductivity Center,
Internal report No. **36aj.**

SSCL/Industry Technology Transfer Presentation F.1.2

Superconducting Materials:
FABRICATION AND PROCESS VARIABLES by *P. J. Lee*

Presented June 17th 1991, Dallas, TX. This version adapted and updated for "Applied Superconductivity," a Fall semester 1992 class at the University of WI-Madison.



TEM Micrograph of a Transverse Cross-Section
of a Nb-47wt.%Ti Filament at Peak Final Strain

Applied Superconductivity Class

Outline

III. FABRICATION AND PROCESS VARIABLES.

(P. J. Lee, Applied Superconductivity Center U.W.-Madison)

A. Overview of Baseline process:

1. Outline of Conductor Fabrication Steps.
2. Critical Process Variables
   and their Influence on Final Product.

B. Unresolved Issues.

A. Overview of Baseline process:

1. Outline of Conductor Fabrication Steps.

    1.1 Strain Space.

    1.2 Intrinsic Properties and Extrinsic Limitations.

A.1.1 Strain Space

Extremely High Level of Cold Work Strain Required

Strain normally expressed as
True Strain,

$$\varepsilon_t = \ln \frac{A_o}{A} = 2\ln \frac{D_o}{D}$$

where A_o and D_o are original transverse cross-sectional area and diameter respectively, and A and D are the final cross-sectional area and diameter respectively after the strain has been applied.

The Total Available Strain Space can thus be defined as:

$$\varepsilon_{sp}=\ln\frac{A_R}{A_w}=2\ln\frac{D_R}{D_w}$$

where A_R and D_R are the Nb-Ti rod/ingot cross-sectional area and diameter respectively, after final recrystallization anneal and A_w and D_w are the final filament cross-sectional area and diameter respectively.

. In general the larger the strain space the higher the J_c.

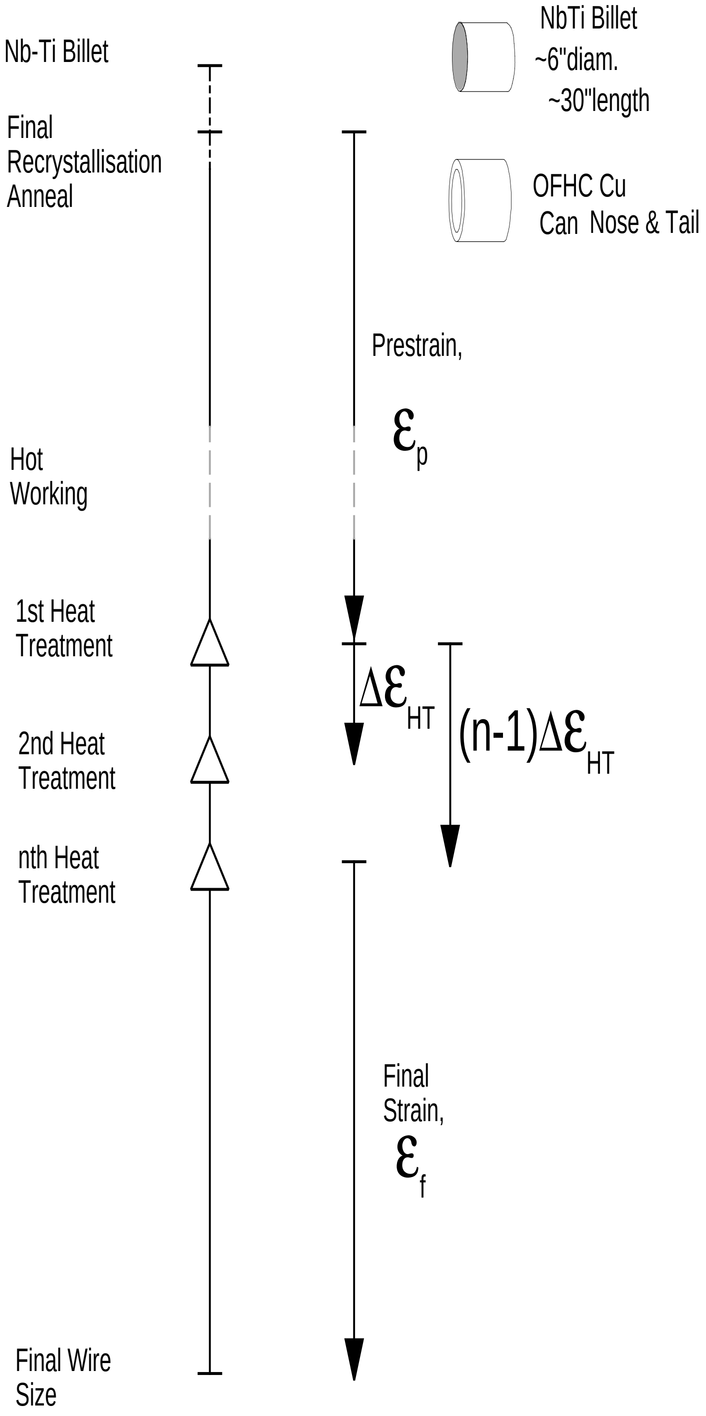


Figure 2 The wire fabrication process can be illustrated in terms of this strain space.

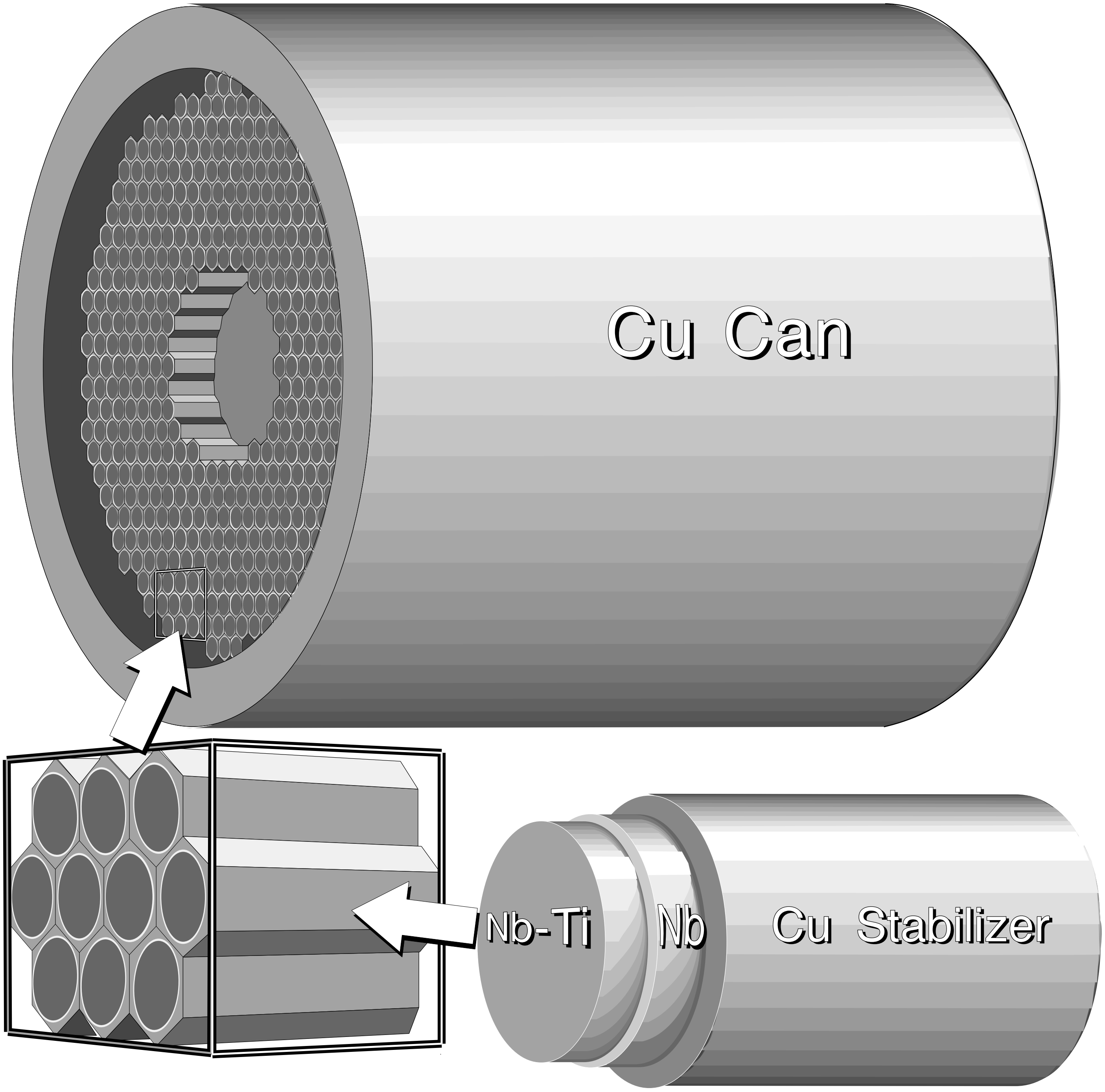


Figure 3 Schematic Illustration of Multifilamentary Billet Assembly

- The *Effective* cold work strain space is reduced by intermediate <u>hot working</u> i.e. *warm extrusion*. The amount of cold work lost during a hot working process such as extrusion has not been quantified.

A.1.2 Intrinsic Properties and Extrinsic Limitations

- The *Intrinsic properties* of the superconductor are those attributable to the chemical and microstructural state of the superconducting material.

- The *Extrinsic limitations* are those macroscopic properties of the conductor that reduce the superconducting properties from the upper limit set by the intrinsic properties. The major extrinsic limitation is the variation in filament diameter ("*sausaging*").

The high intrinsic J_cs of Nb-Ti filaments are obtained by creating a dense array of α-Titanium precipitates in the β-Nb-Ti matrix that is close in scale to the equilibrium fluxoid spacing.

Intrinsic Properties-Microstructural Objectives

1. Maximum Volume of Precipitate. - J_c increases linearly with Volume of precipitate (Figure 4).

2. Avoidance of other precipitate morphologies. - ω-phase and Widmanstätten α-Ti increase hardness (reduce draw-ability) and produce precipitate size inhomogeneity.

3. Homogeneous Precipitate Distribution and Size. - to maximize flux-pinning at optimization strain.

Unresolved -Ideal Precipitate Size
-May vary with field
-May be different for APCs

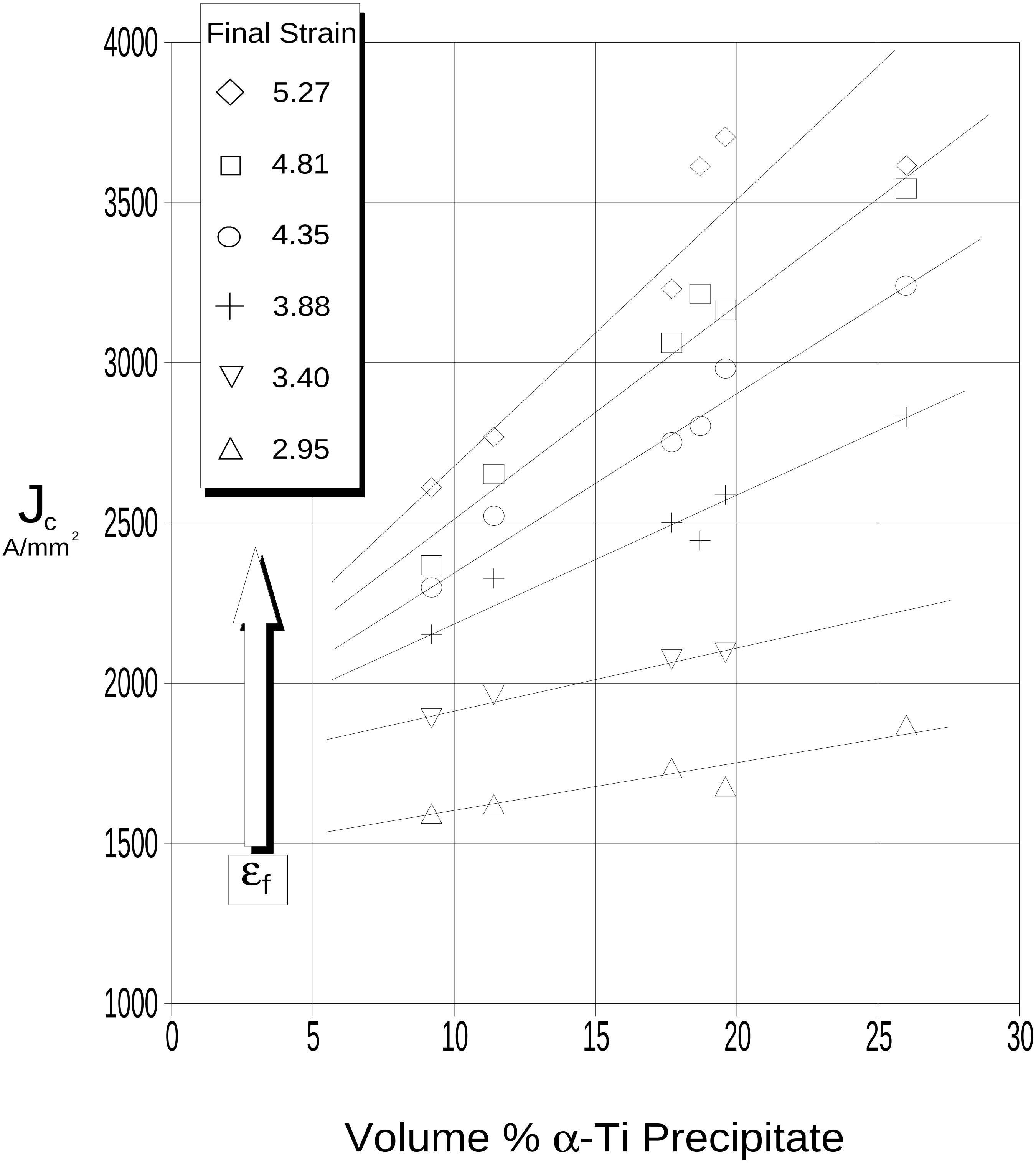


Figure 4 Critical current density at 5T, 4.2K versus volume % α-Ti precipitate for a range of final cold drawing strains.

A.2. Critical Process Variables and their Influence on Final Product.

Development of High *Intrinsic* J_c -*Microstructural Viewpoint*

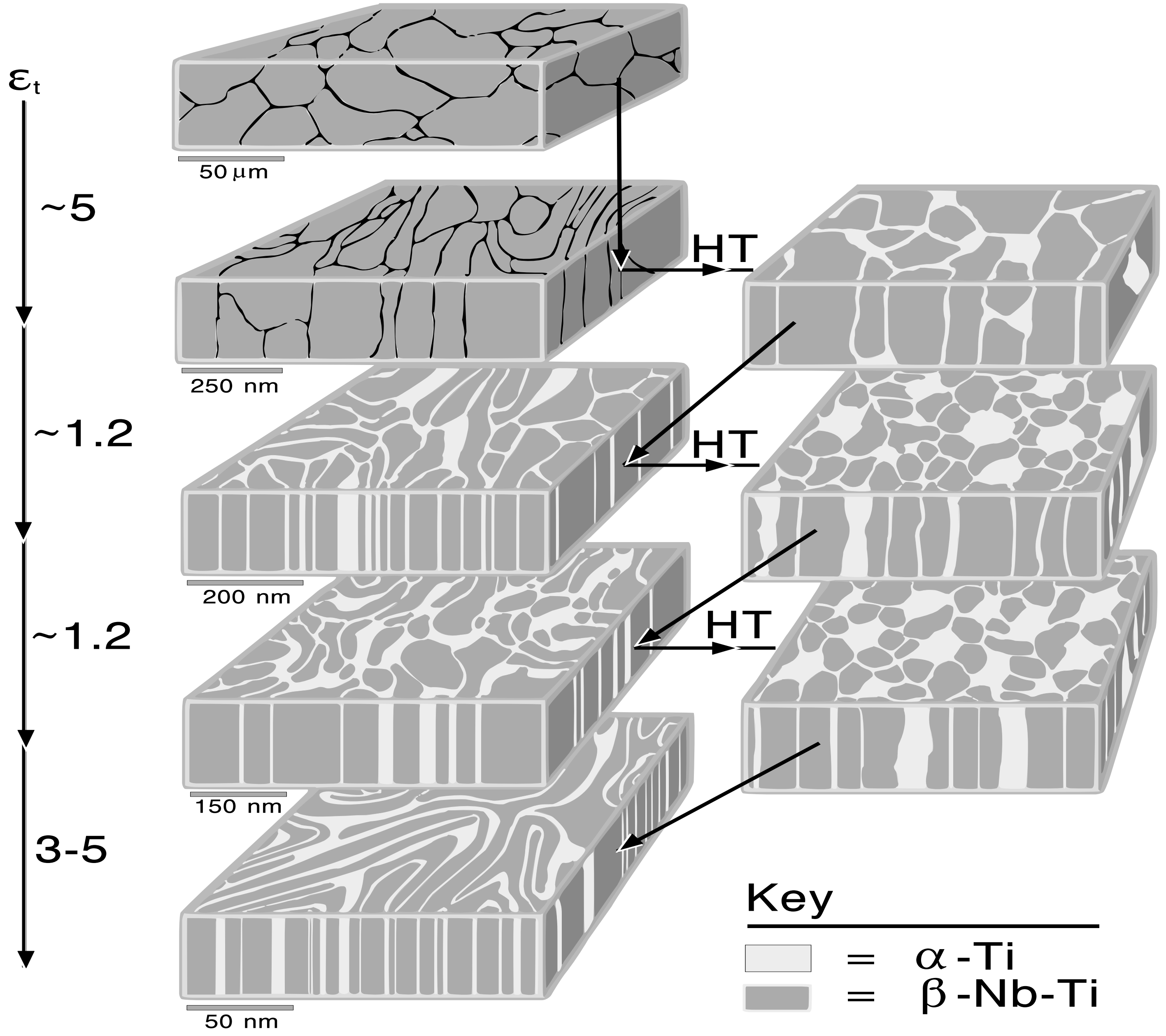
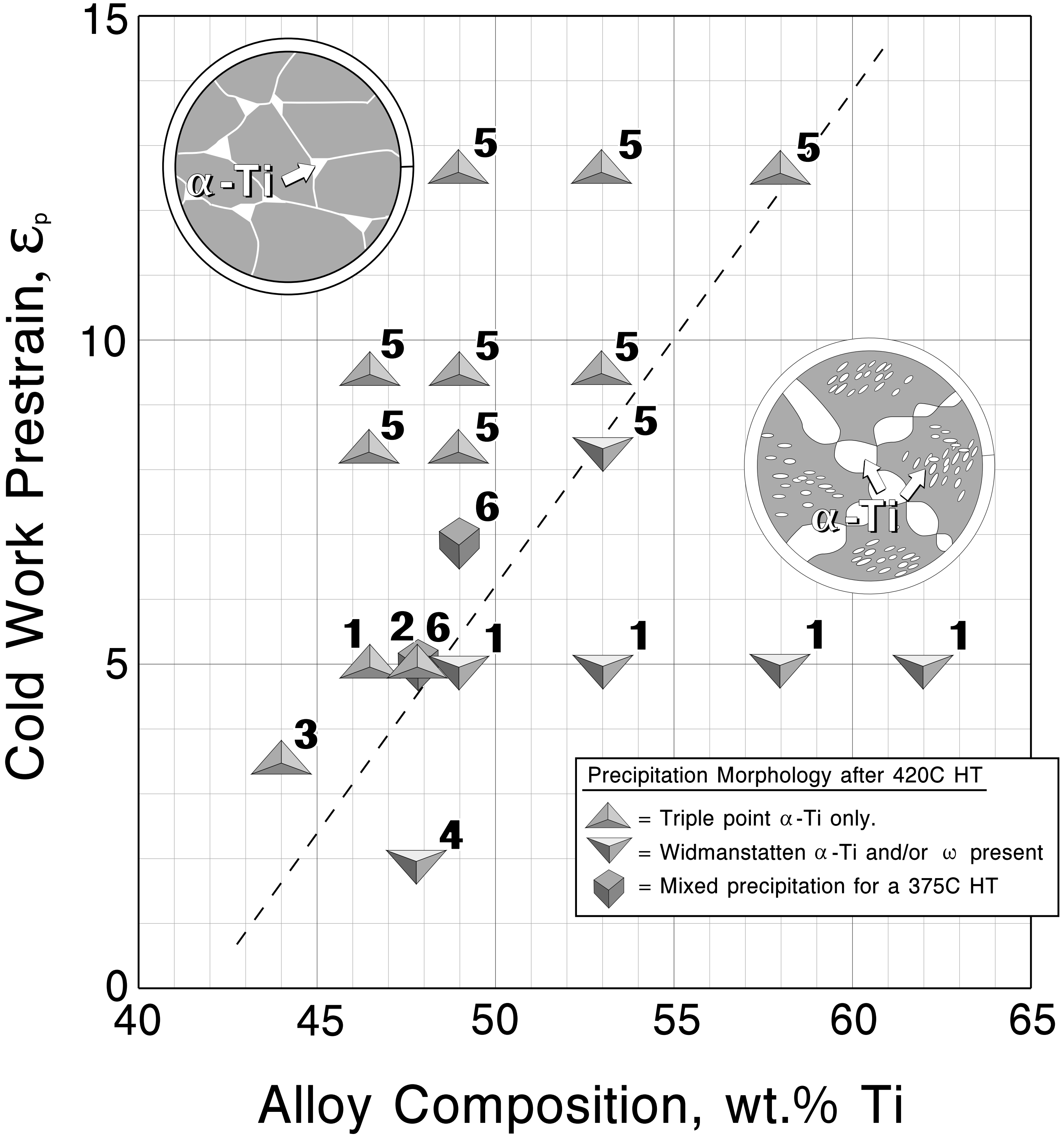


Figure 5 Development of high *intrinsic* J_c.

2.1 Alloy Fabrication

Figure 5-Step 1. **Alloy at Zero Strain**

High Homogeneity.	Uniform Precipitate Morphology. Uniform Precipitate Size and Distribution. Uniform Draw-ability. Maximum Ductility.
Figure 6.	Alloy Composition vs Cold Work Strain & Precipitate Morphology.
Figure 7.	Alloy Composition vs. Precipitate Volume.
Fine Grain Size	Maximize Precipitate Nucleation Sites. Maximize Cold Work Strain.
Good Surface Finish	Improve Bonding with Nb Wrap.



1 = Lee, Larbalestier & McKinnell, Adv.Cryo.Eng. (1988), 2 = Lee & Larbalestier, Acta Met. (1987),
3 = Lee, Larbalestier & McKinnell, New Dev. in Appl. Superconductivity (1988),
4 = Buckett & Larbalestier, IEEE Trans. Mag., (1987),
5 = McKinnell, Lee, Remsbottom, Larbalestier, O'Larey, McDonald, Adv. Cryo. Eng. Mat. (1988),
6 = Lee, McKinnell & Larbalestier, University of WI-Madison, unpublished

Figure 6 Alloy Composition vs Cold Work Strain & Precipitate Morphology.

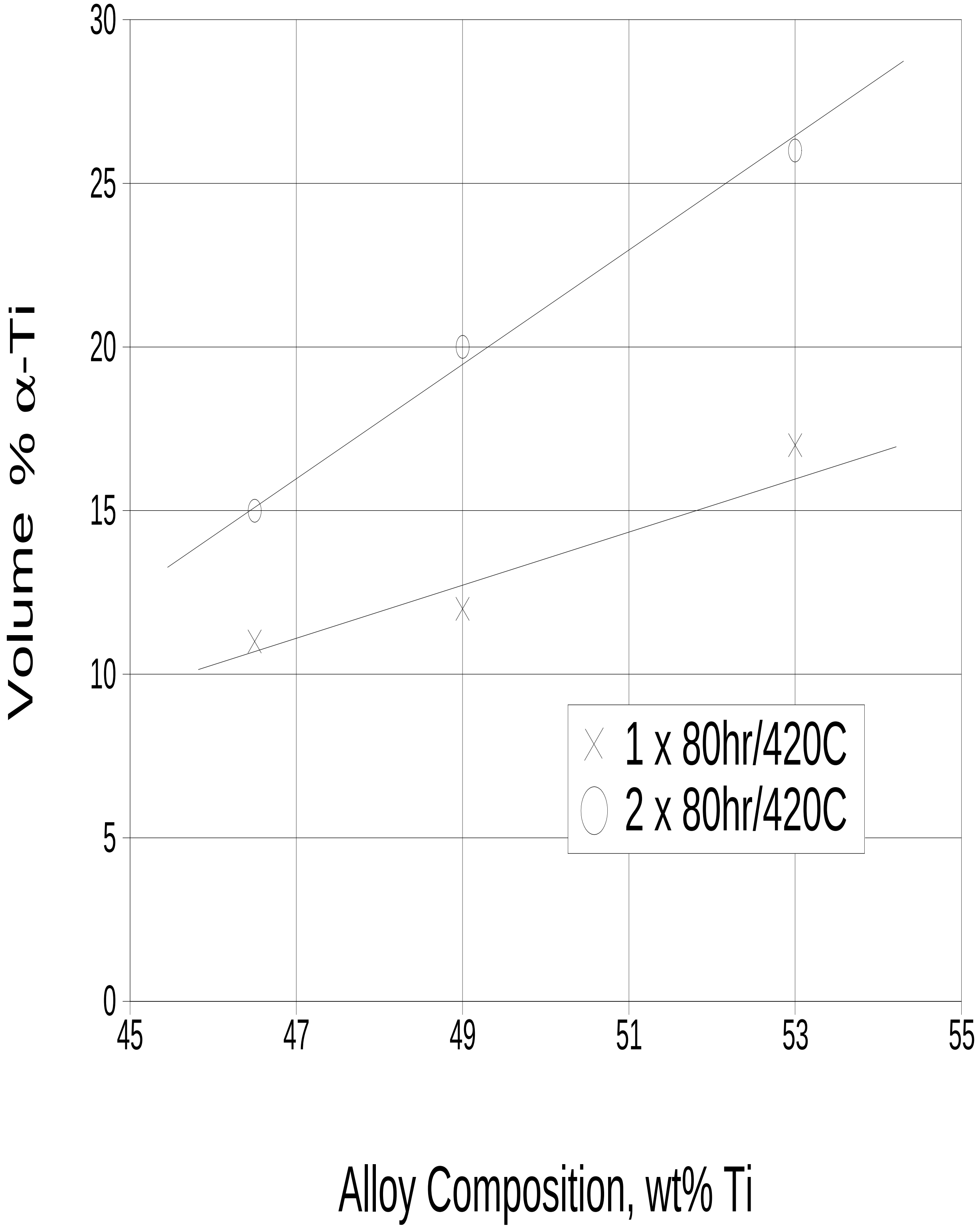


Figure 7 Alloy Composition vs Precipitate Volume.

Additional notes on alloy homogeneity

Alloy Fabrication - Alloy Homogeneity

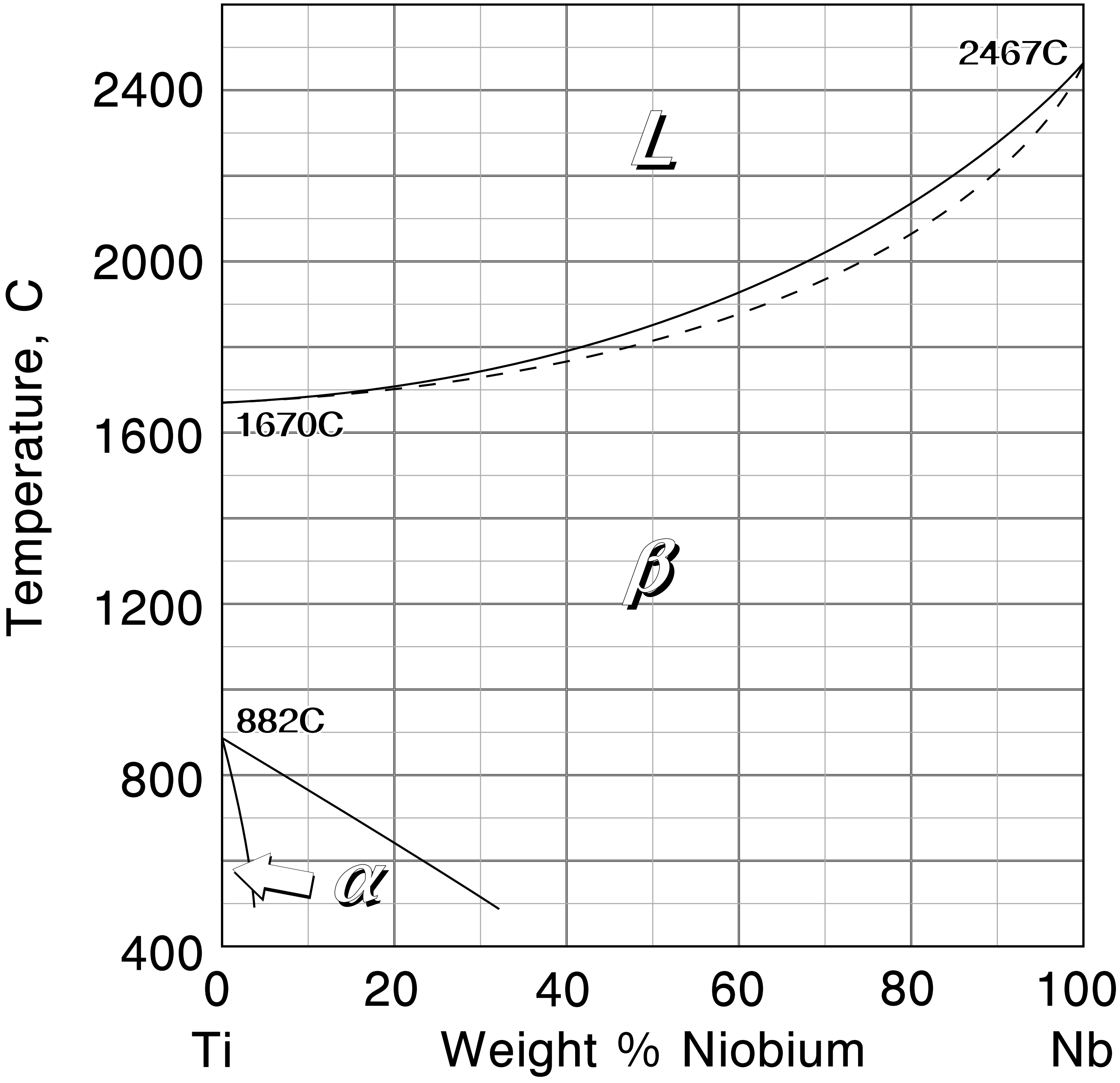


Figure 8 Niobium-Titanium Phase Diagram (after J. L. Murray, “The Nb-Ti (niobium-titanium) system,” *Bulletin of Alloy Phase Diagrams*, Vol. 2, pp. 55-61, 1981.

Coring. Large Difference in Freezing Points of Nb(1670C) and Ti(2467C) can result in localized solute enrichment if the process is not properly controlled. Good quality alloy has a local compositional variation of less than 1.5 wt%Ti.

Nb-rich Inclusions. Typically from too low a current during melting, these are particularly dangerous when made hard by reaction of the Nb drips with interstitials.

Ti-rich "Freckles". Produced by interdendritic flow of solute rich material. Although there is no direct correlation between freckles and poor wire performance a lack of freckles normally means that there has been good control of radial heat transfer and fluid flow in the melt pool. Freckles are easy to spot in *Flash Radiographs* and thus a lack of "freckling" is regarded as an economical standard to adopt.

Surface Enrichments. Chill zone at edge of ingot may have higher Ti content. With large scale ingots these areas can be machined off. Manufacturers with smaller ingot size do not have the same flexibility.

2.2 Composite Assembly

See Figure 3

2.2.1 Cleanliness, Surface Quality, and Bonding

Uniform drawing requires good metallurgical bonding of components-requires surfaces as clean as practically possible.

Small hard particles picked up by components will not co-draw and will have a disastrous effect on final wire drawing. -most of the recent SSC breakages have been related to this!

2.2.2 Intermetallic Formation and Diffusion Barriers

Cu reacts with the Ti to produce a hard non-drawing intermetallic at the Cu-superconductor interface.-This was the main cause of non-uniform filament drawing until Nb-diffusion barriers were introduced.

Unresolved Issues

Optimum Barrier Thickness

Barrier thickness is a trade-off between lost superconductor volume and degree of barrier breakdown.

Barrier Application

Single versus multiple wraps.
Texture orientation.
Barrier purity and grain size.

2.2.3 Composite Design to Minimize Drawing Instability

S/D Ratio

The filament spacing to diameter ratio is critical to good wire drawing. The smaller the better (typically 0.13-0.17) but...

Almost Resolved Issue..
The designed S/D ratio is a trade-off between draw-ability and filament proximity-effect coupling. Too small a filament spacing will result in adjoining filaments behaving as one in terms of superconducting behavior (more on this tomorrow-Ghosh). This problem increases with decreasing filament size. For fine filaments (<3-4μm) this can be overcome by alloying additions (Mn) to the copper.

Copper Distribution

Some manufacturers think it is better to put a lot of Cu into a Cu core, some don’t. The idea is to reduce “centreburst” during extrusion.

2.2.4 Extrusion

Extrusion temperature, rate, preheat.

All very much wire a manufacturers trade secret.

Temperature	Increasing temperature increases bonding and ease of extrusion **but** reduces effective prestrain for precipitation.
HIPing	Hot Isostatic Pressing prior to extrusion can increase bonding prior to extrusion to allow lower extrusion temperatures.

2.3 Heat Treatments

(Figure 5 Step 2).

Condition of Nb-Ti Prior to First Heat Treatment

High Prestrain -	Ensures Optimum Precipitate Morphology (Figure 6). Maximizes Precipitate Quantity.

(Figure 5 Steps 3,5,7).

Precipitation Heat Treatments

2.3.1 Aims of Heat Treatments

Maximize Volume of Precipitate.
Minimize Precipitate Growth.
Minimize Cu-Superconductor interdiffusion.

Conditions

Temperature	≥375C to produce sufficient α-Ti ≤420C to minimize α-Ti growth.
Time -	≥ 40hrs to produce sufficient precipitate.
Number -	≥3 to produce sufficient precipitate.

(Figure 5 Steps 4,6).

Inter-Heat Treatment Strain Increment

Strain Increment - > 0.69 (3 std. dies) to be effective.
< 1.15 (5 std. dies) for efficient
use of strain space.

2.3.2. Influence of H.T.s on Intrinsic Properties.

Increase J_c with volume of α-Ti. Minimize ε_f to peak J_c by minimizing precipitate size.

2.3.3 Influence of H.T.s on Extrinsic Limitations.

Increase Cu/Sc interdiffusion - mostly with temperature increases.
Cu/Sc hardness difference increased-
Softening of Cu inevitable,
hardening of Nb-Ti can be reduced by avoiding ω-phase and Widmanstätten α-Ti.

2.4 Wire Drawing

(Figure 5 Step 8).

Final Strain

Magnitude - > 4 to produce sufficiently dense precipitate array.
< 6* to avoid over reduction of precipitates.

*= never achieved in SSC composites.

2.4.1 Die scheduling, Design and Maintenance

Die scheduling and design (e.g. angle) are commercial secrets for the wire manufacturers. Computer models are now available (Avitzur-Lehigh) for trimetallic systems like this but not all the parameters are known.

Die maintenance (including avoidance of build up on dies during drawing and inspection of dies for damage) is important for producing both uniform wires and filaments.

2.4.2 Preparation for Cabling.

Cu anneals are sometimes requested by magnet designers in order to reduce the resistivity of the now heavily cold-worked Cu and sometimes to ease cabling (this is not necessarily the case), these anneals normally decrease the J_c of high J_c composites and alter the J_c versus Field slope.

Twisting of the composite is required to reduce flux-jump and eddy current losses, the degree of twisting is an unresolved issue, reducing the twist reduces J_c degradation and makes wire manufacturers happy, it also makes magnet manufacturers nervous (the minimum twist pitch required is an unknown.