Aging Heat Treatments of Ti-Nb and Ti-Nb-Sn Alloys

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Campinas, SP, Brazil

University of Campinas

- **Founded in 1966**
- **Strong tradition in education and in scientific research (15% of the Brazilian Scientific Production)**
- **17,000 undergraduate and 16,000 graduate students**

Outline

- Motivation to Study Ti Alloy Phase Transformations
  - Materials for Implant
- Ti Alloys Phase Transformations
- Experiments
- Results
  - Metastable Phase Formation: JEQ Experiments
  - Metastable Phase Decomposition: DSC, HTXRD
  - Aging Heat Treatment and Mechanical Behavior
  - Applications

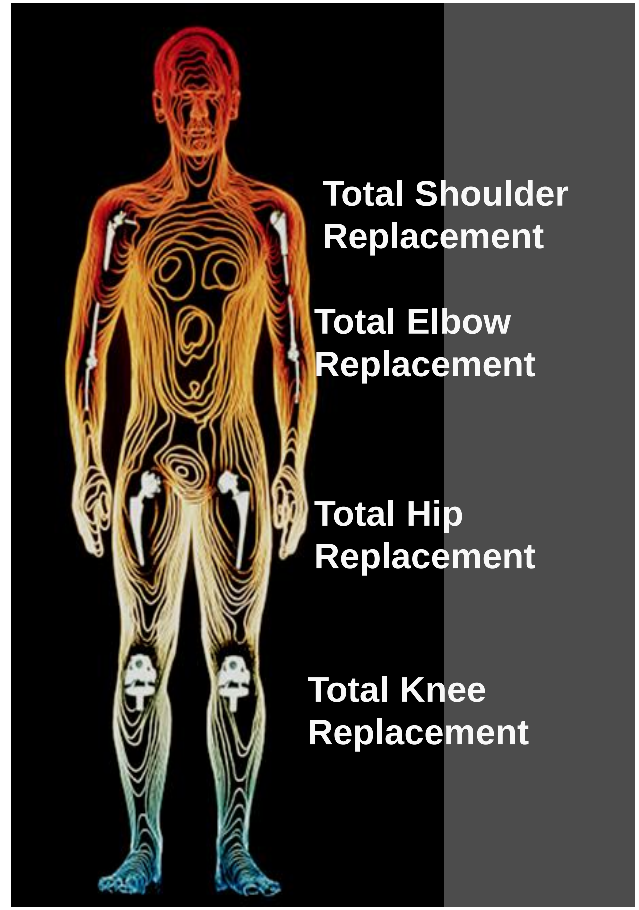
Orthopedic Biomaterials

- Biomaterials market is estimated to be worth more than US$ 300 billion and to be increasing 20% per year
- Orthopedic and dental applications represent 55% of the biomaterials market
- 2010:
  - More than 4.4 million people with at least one internal fixation device
  - 1.3 million people with an artificial joint

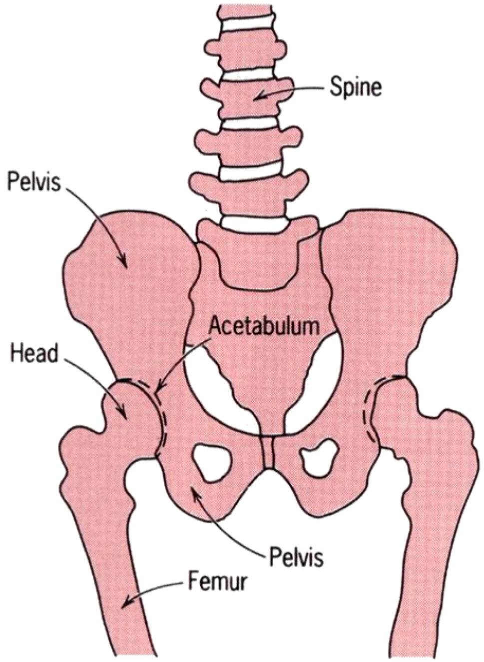
Nanomedicine: Nanotechnology, Biology and Medicine 7 (2011) 22–39

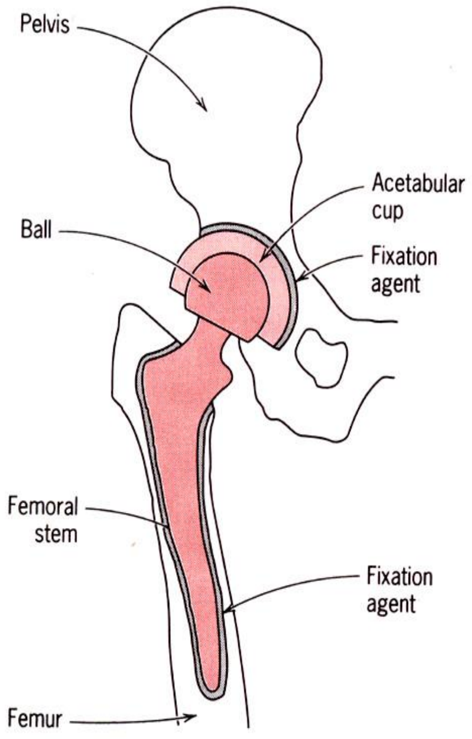
Total Joint Replacement

- **TJR surgical procedure: parts of a damaged joint are removed and replaced with prostheses**
- **Prosthesis is designed to enable the artificial joint to move just like a normal healthy joint**



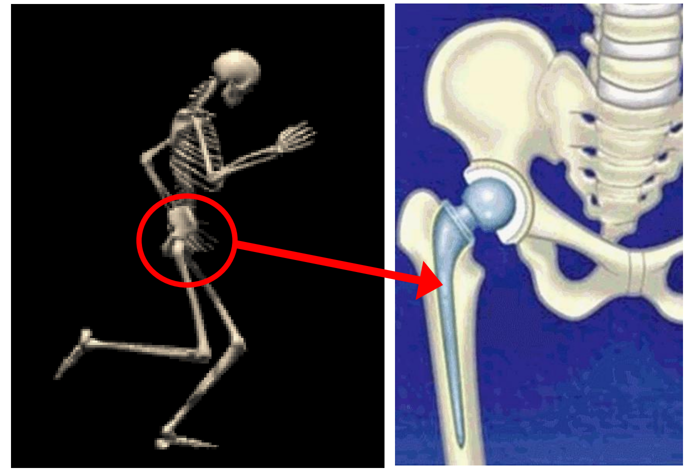
Total Hip Replacement





Bone Deformation

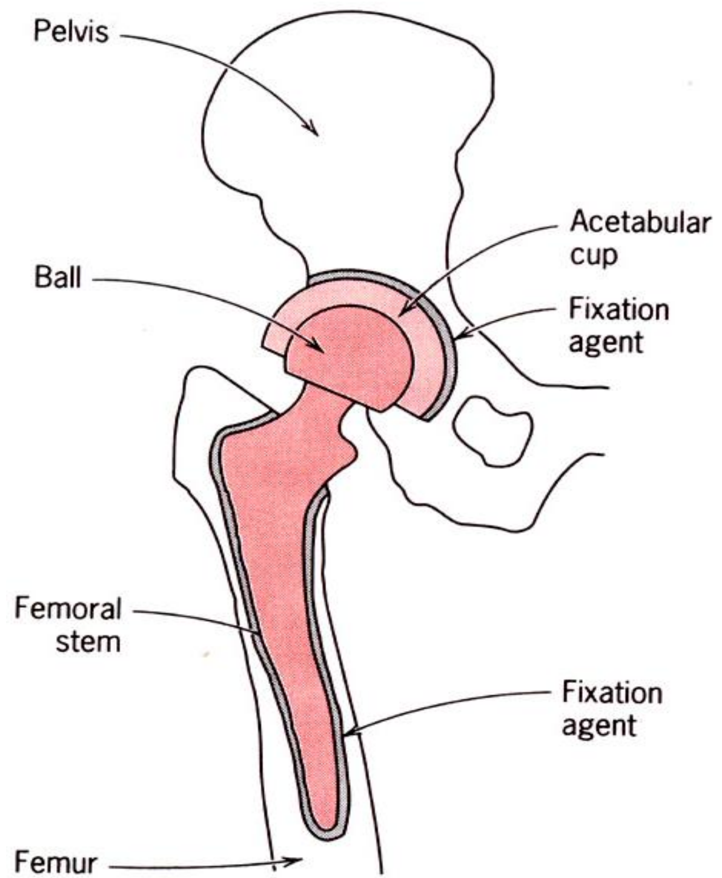
- **Implant material must simulate bone elastic behavior**
- **Insufficient load transfer from the implant to the bone causes bone re-absorption and loosening of the implant**
- **Reduction of load applied to the bone causes bone mass loss and osteoporosis**



316L Stainless Steel
E = 200 GPa

Total Hip Replacement

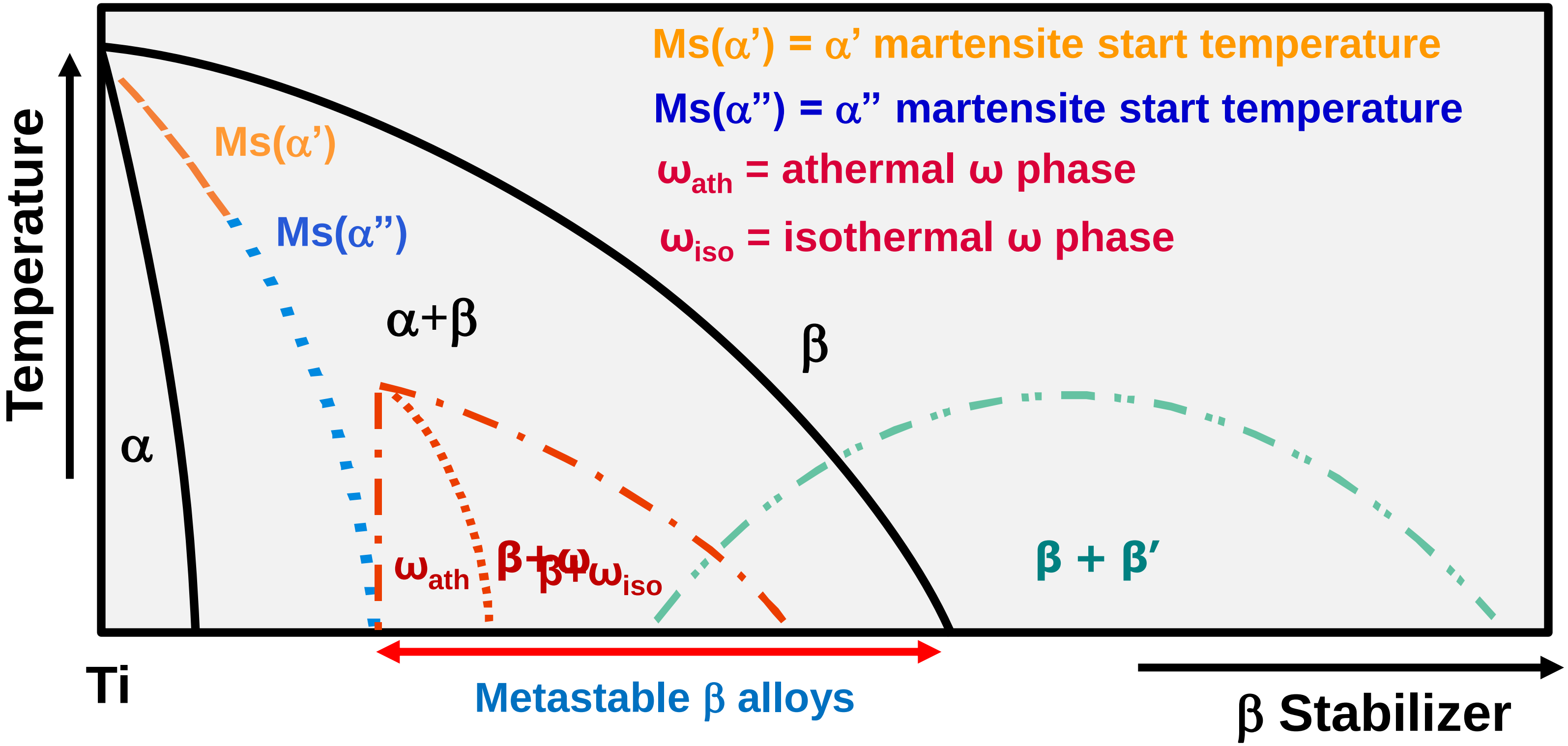
- **Femoral Stem:**
  - **Mechanical strength**
  - **Biocompatibility**
  - **Corrosion resistance**
  - **Bone elastic behavior**
  - **Low elastic modulus to avoid " bone stress shielding"**
    - E_{bone}: 10 - 30 GPa
    - E_{Ti-CP}: 110 GPa
    - $E_{Ti-6Al-4V}$: 106 GPa
    - $E_{\beta-alloys}$ < 60 GPa



Objectives

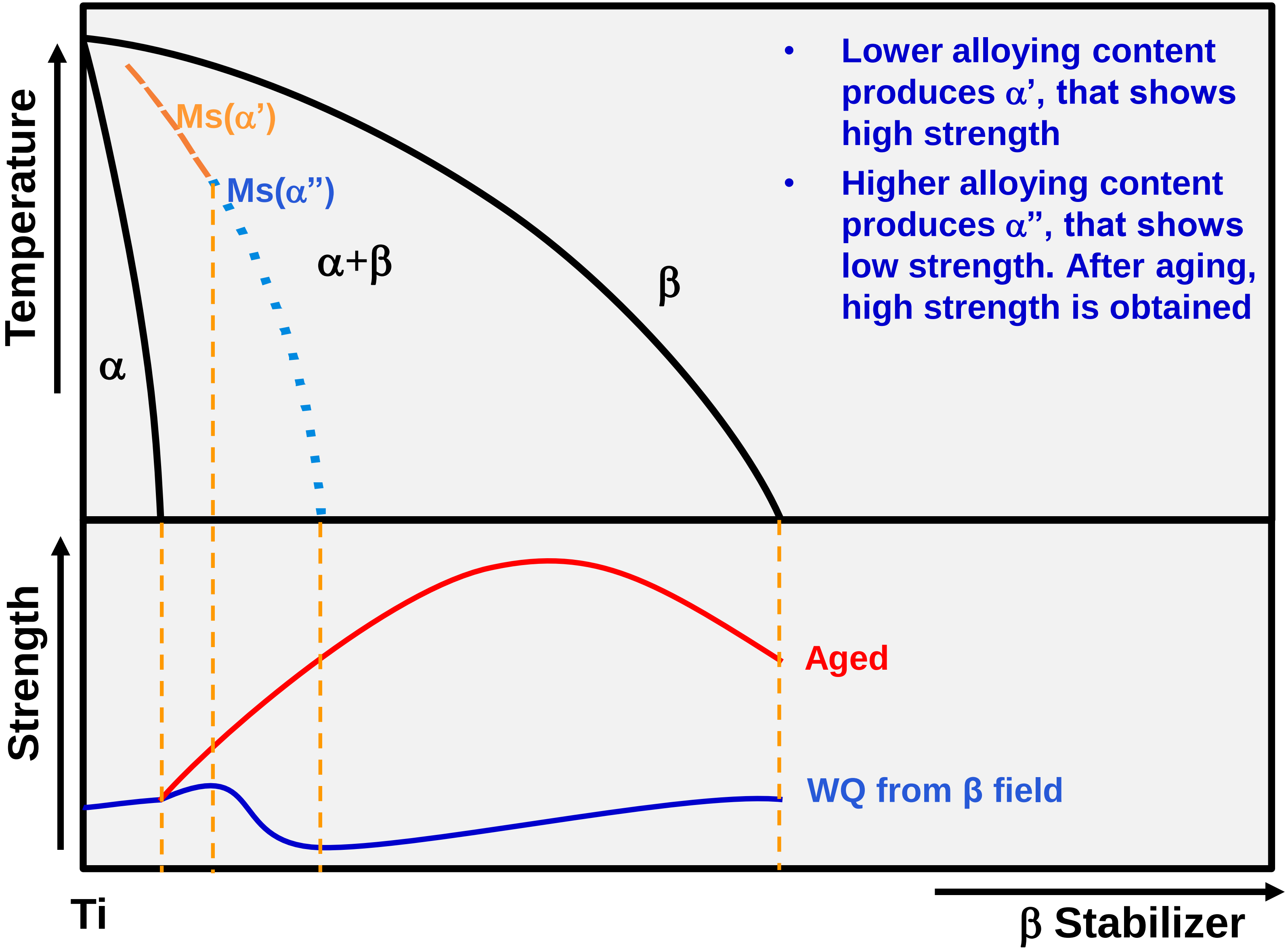
- **To discuss:**
  - **Orthorhombic martensite formation as function of composition and cooling rate**
  - **Phase precipitation during aging heat treatment**
  - **Microstructure and mechanical behavior**
  - **Application of phase transformations knowledge on Ti-based implants manufacturing**

Phase Transformations in β Ti Alloys



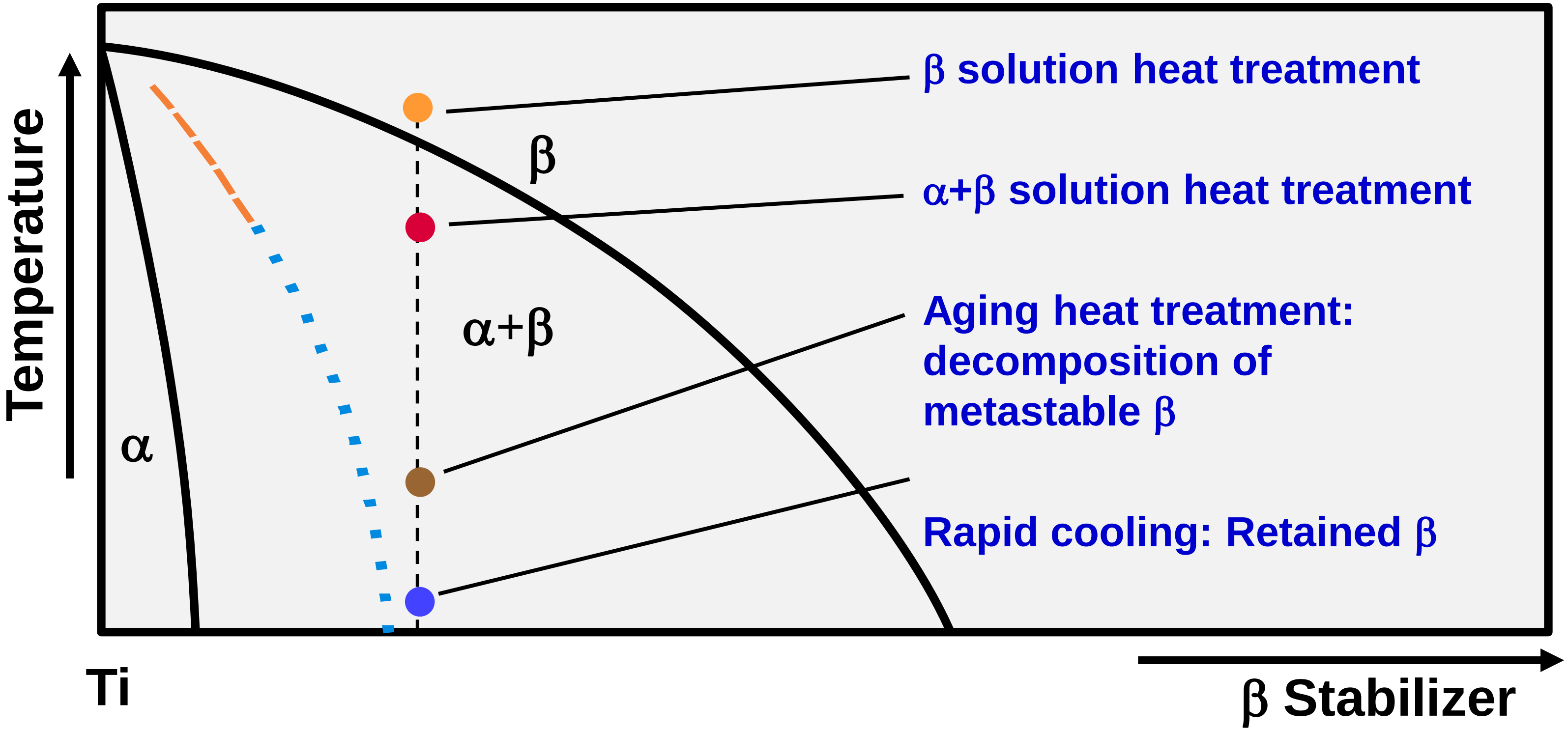
Mestastable Phases

- α" phase: Martensitic phase formed during rapid cooling of β in high solute content alloys
- ω phase: Very small precipitate formed during cooling of β:
  - $\omega_{athermal}$ – formed on quenching, if the solute content is high enough to retain β
  - $\omega_{isothermal}$ – formed during aging in a temperature range of 100ºC to 400ºC
  - ω precipitation - drastic embrittlement of Ti alloys

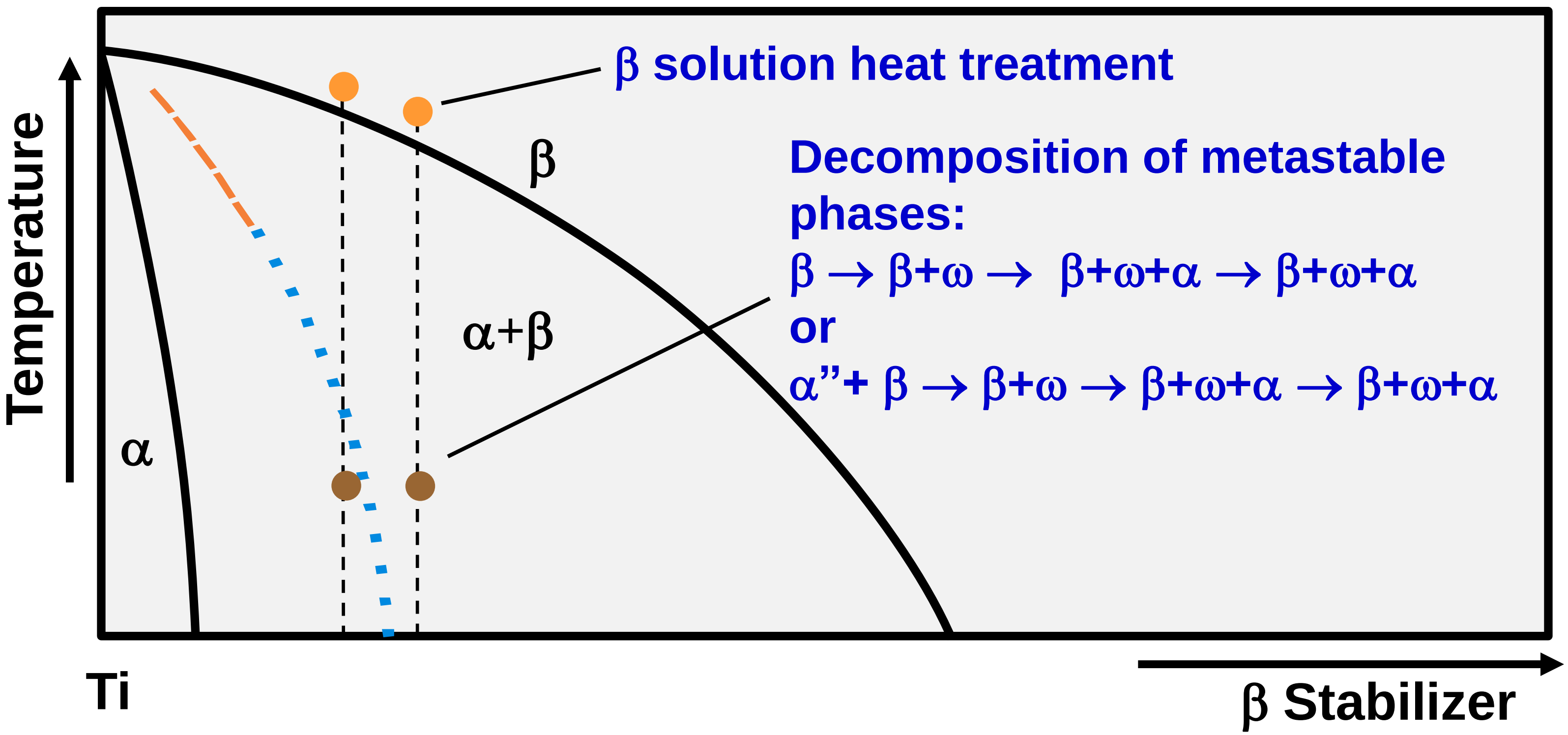


- Lower alloying content produces α', that shows high strength
- Higher alloying content produces α", that shows low strength. After aging, high strength is obtained

Heat Treatment



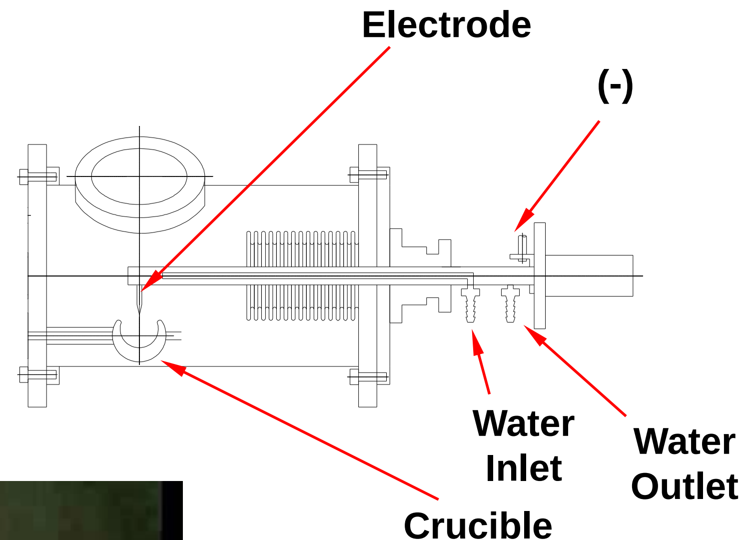
Decomposition of Retained β

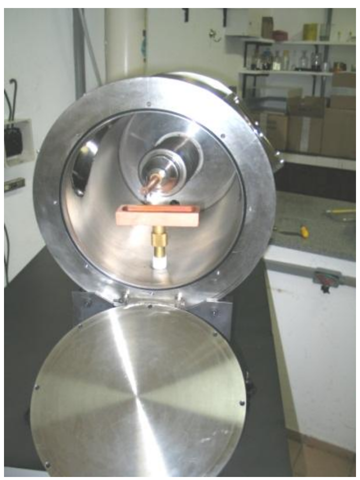


Experiments

Alloy Compositions

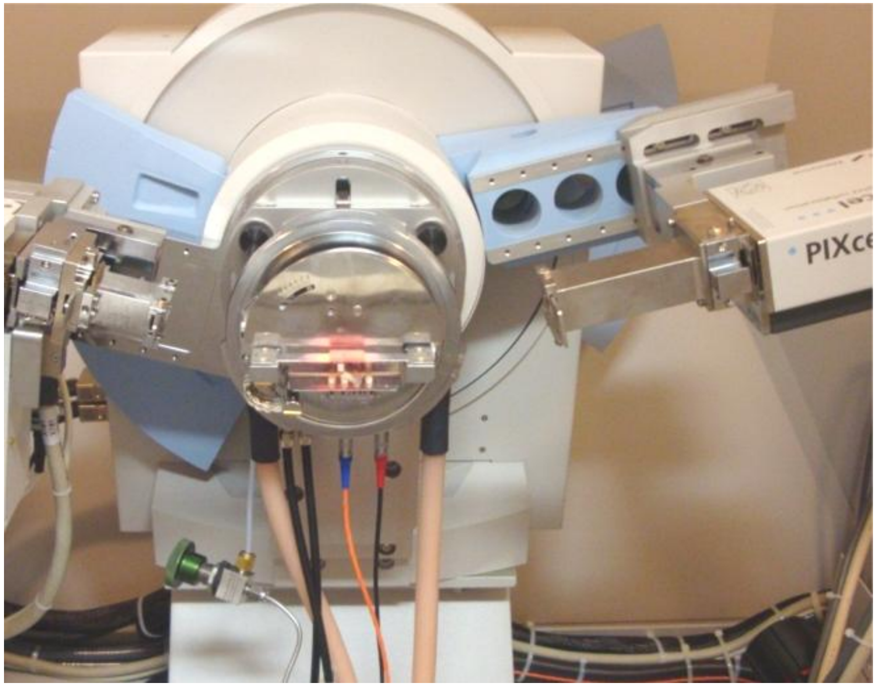
Nominal (wt.%)	Measured (wt.%)
Ti-30.0Nb	Ti-30.4Nb
Ti-30.0Nb-2.0Sn	Ti-30.5Nb-2.1Sn
Ti-30.0Nb-4.0Sn	Ti-30.6Nb-1.9Sn

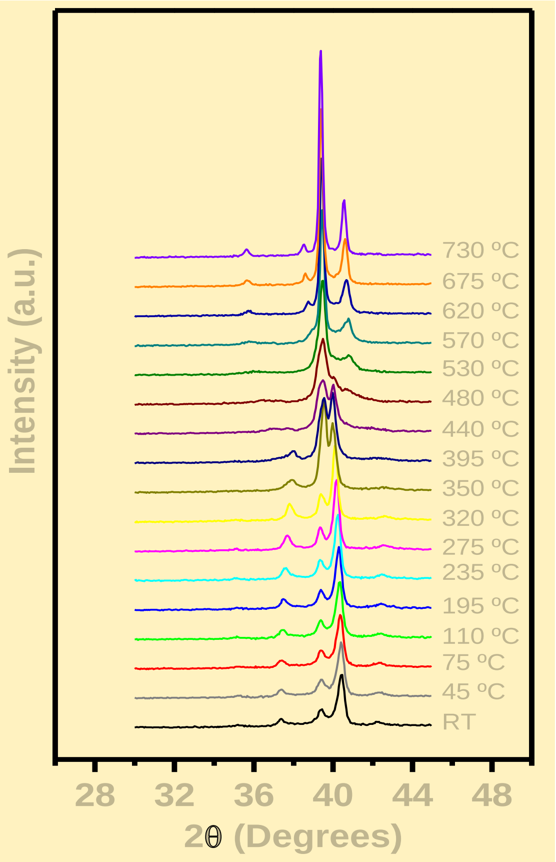




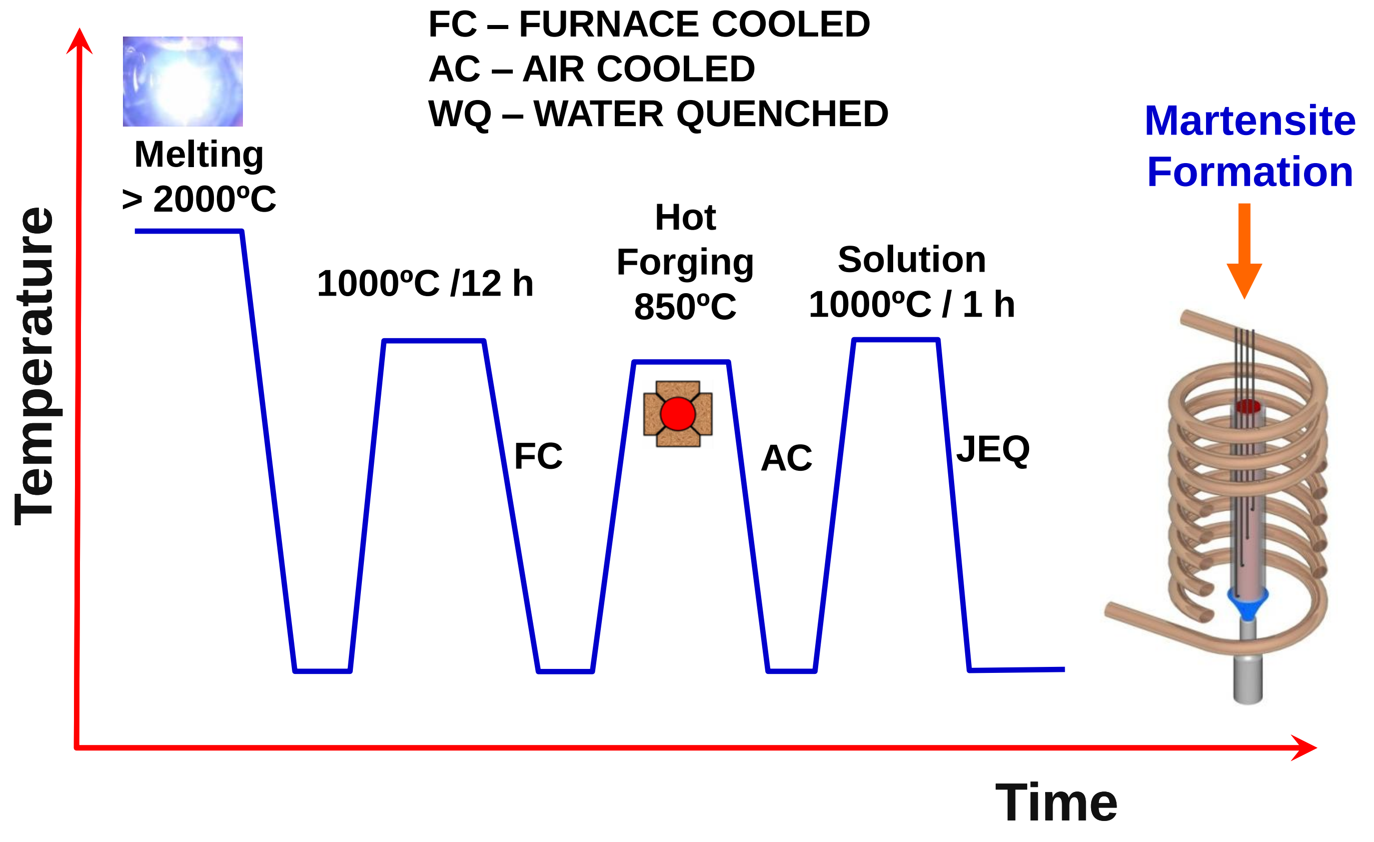
Experiments

High Temperature XRD

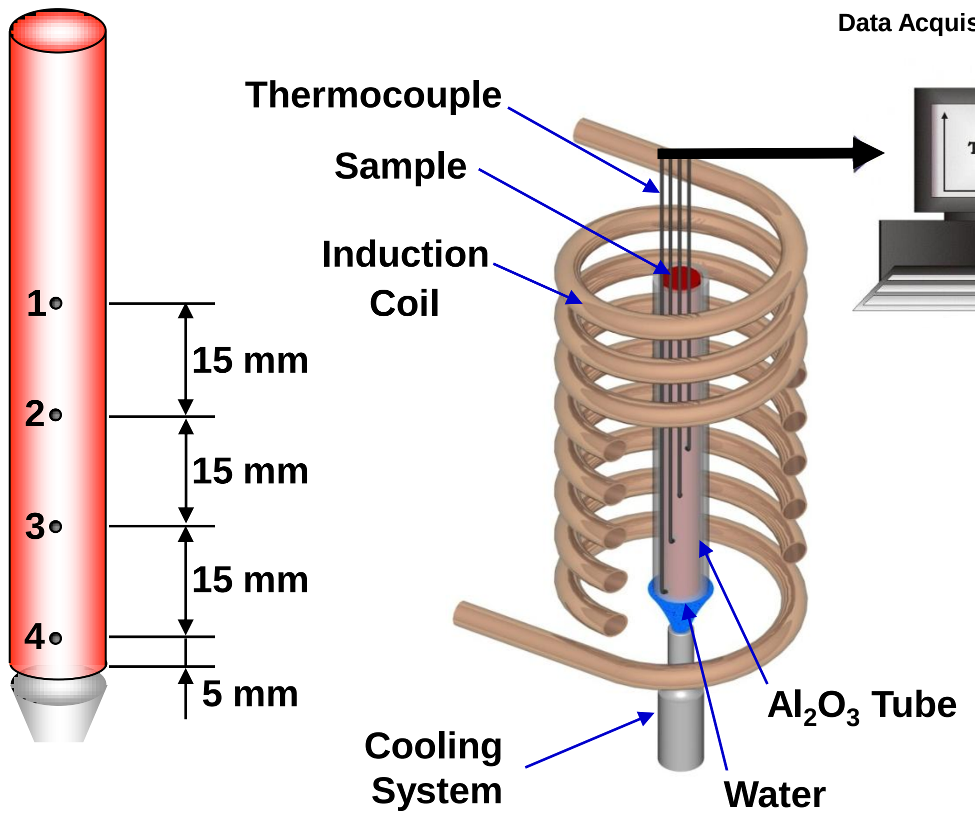


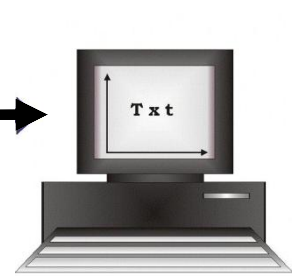


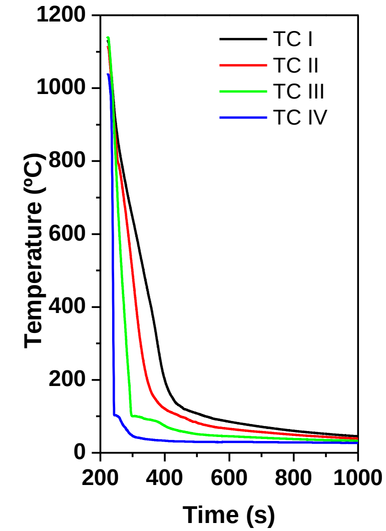
JEQ Experiments

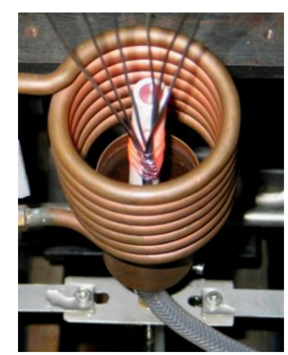


JEQ Experiments

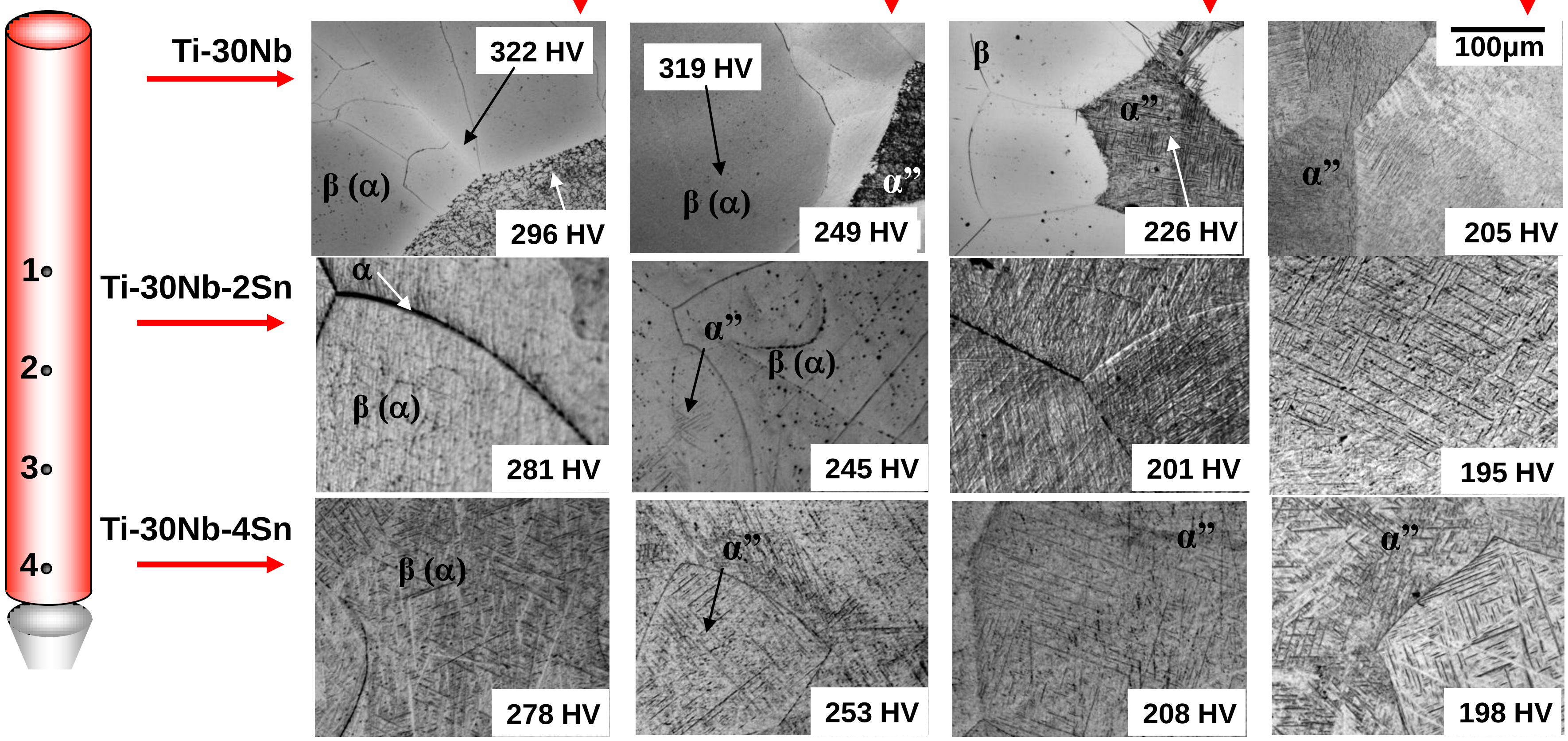






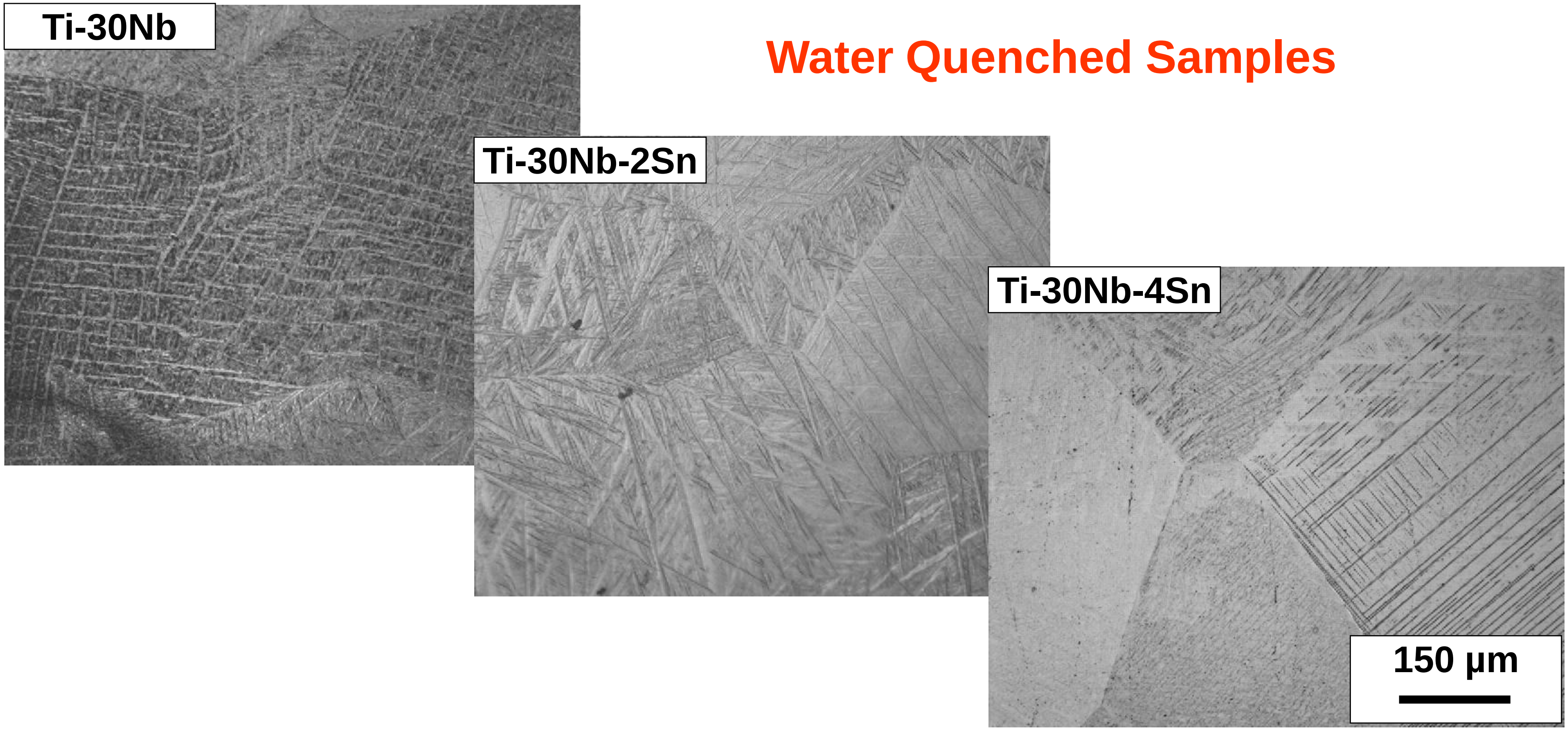


Composition (wt.%)	Cooling Rate (ºC/s)			
	TC1 3.3 – 4.0	**TC2** 7.5 - 8.0	**TC3** 13 - 17	**TC4** 82 - 113
Ti-30Nb	α, β, ω	α, β, α″, ω	β, α″, ω	β, α″, (ω)
Ti-30Nb-2Sn	α, β, ω	α, β , α″	β, α″	β, α″
Ti-30Nb-4Sn	α, β	α, β, α″	β, α″	β, α″

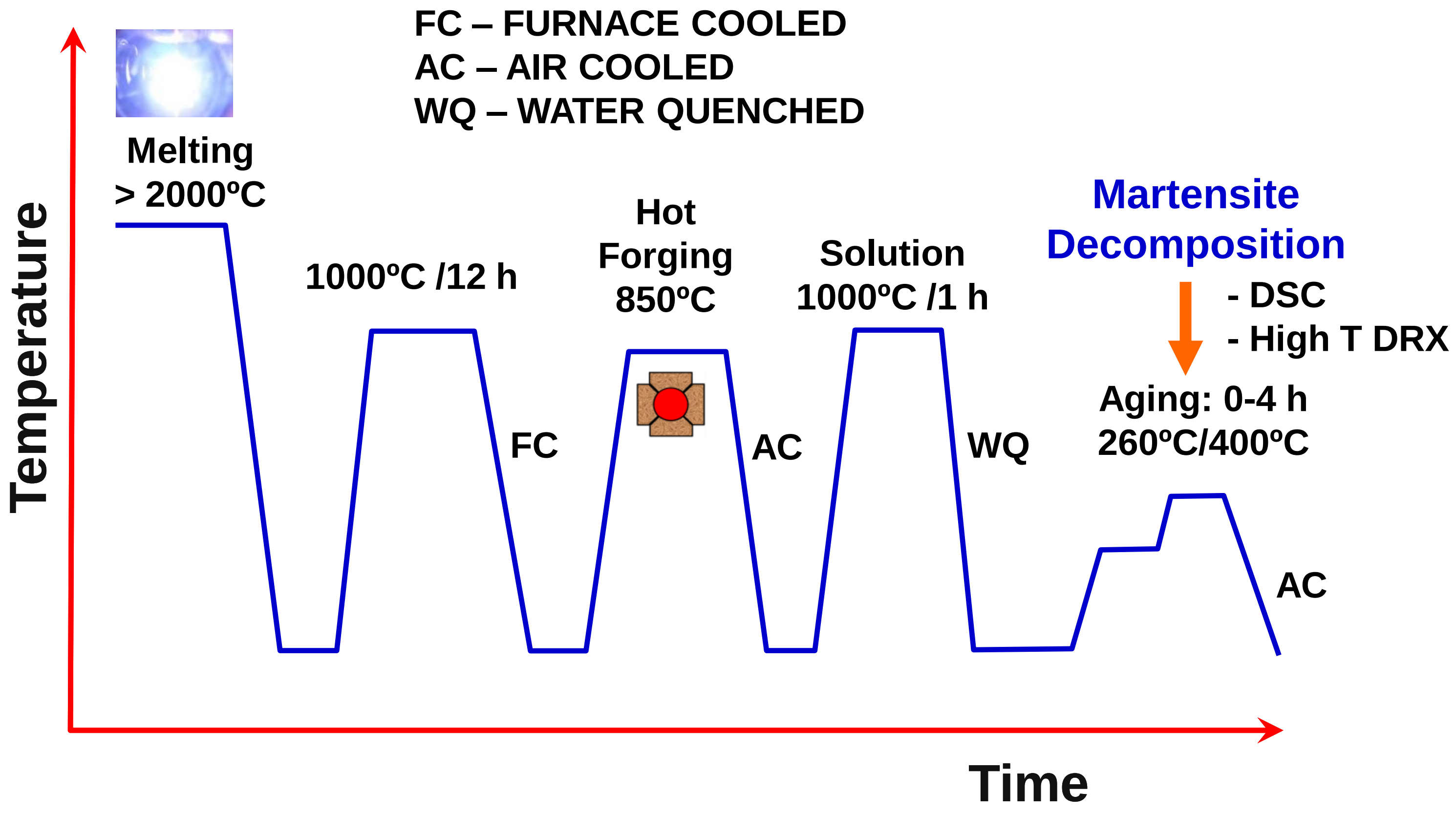


Effect of Sn addition

Water Quenched Samples

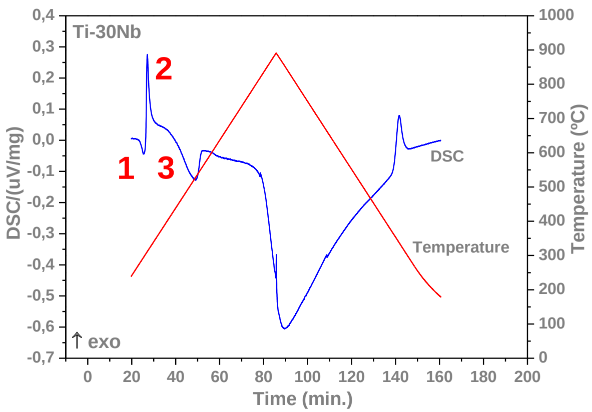


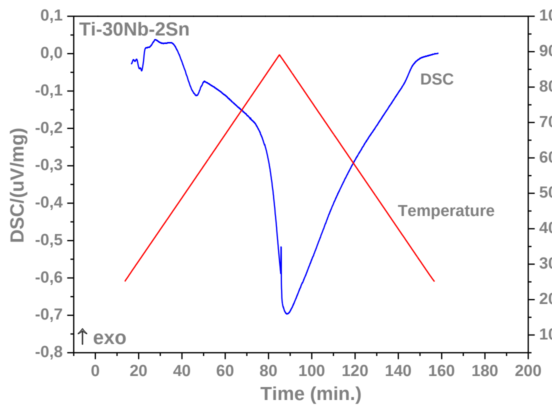
Aging Experiment

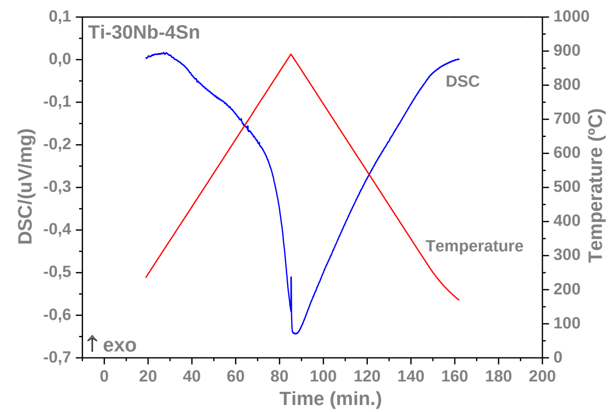


Thermal Analyses

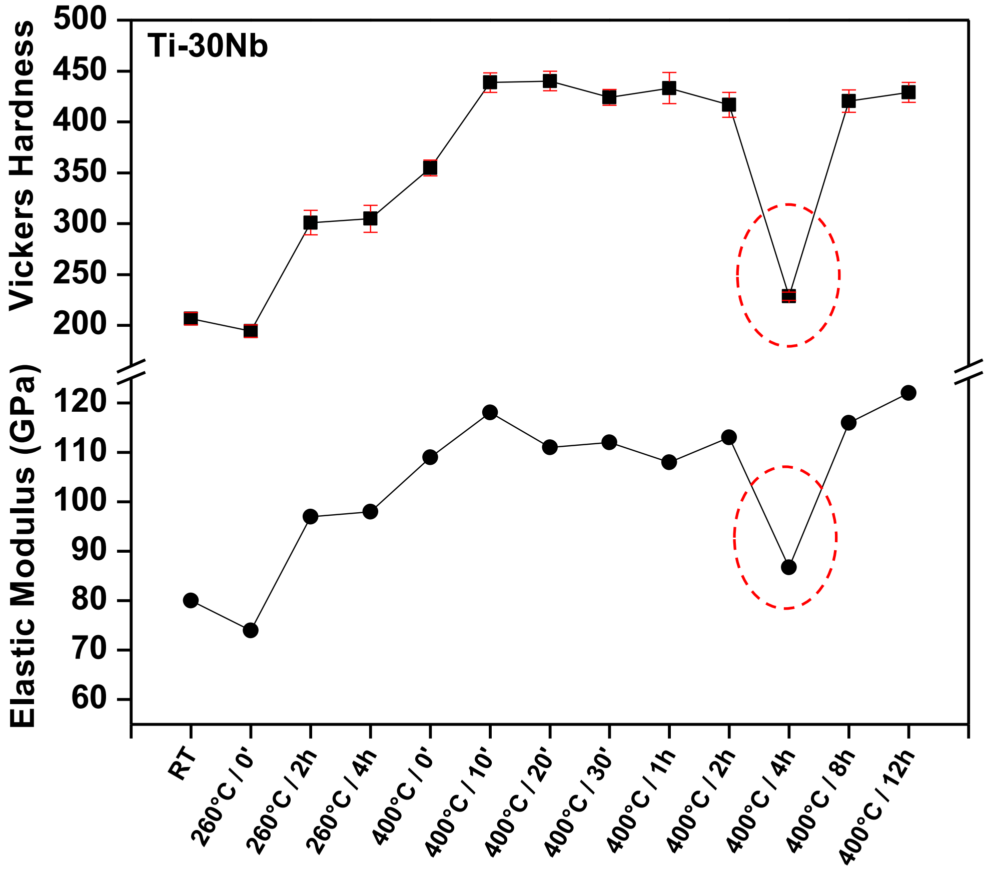
- **DSC of WQ Ti-30Nb sample with α” and β phases showed β decomposition:**
  - **Peak 1: reverse transformation α”→β Precipitation of ω in β matrix (end of peak 1)**
  - **Peak 2: nucleation of α: “ω acts as substrates”**
  - **Peak 3: β transus**







Elastic Modulus and Hardness



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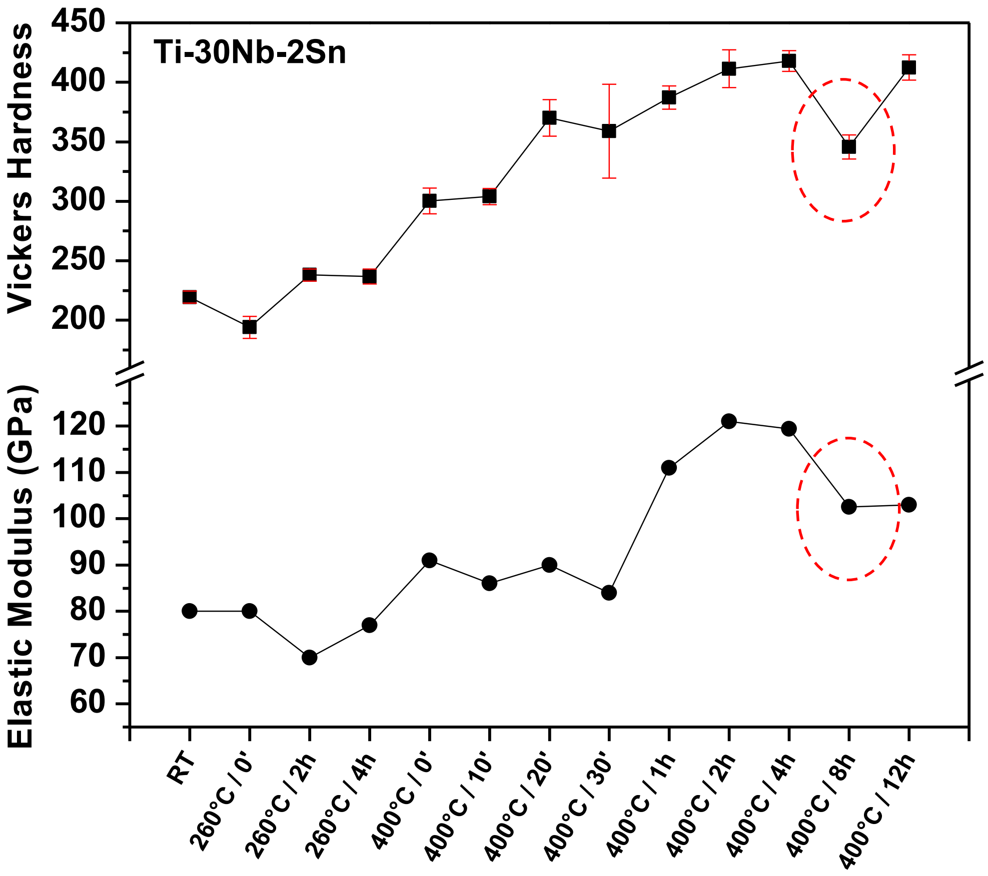
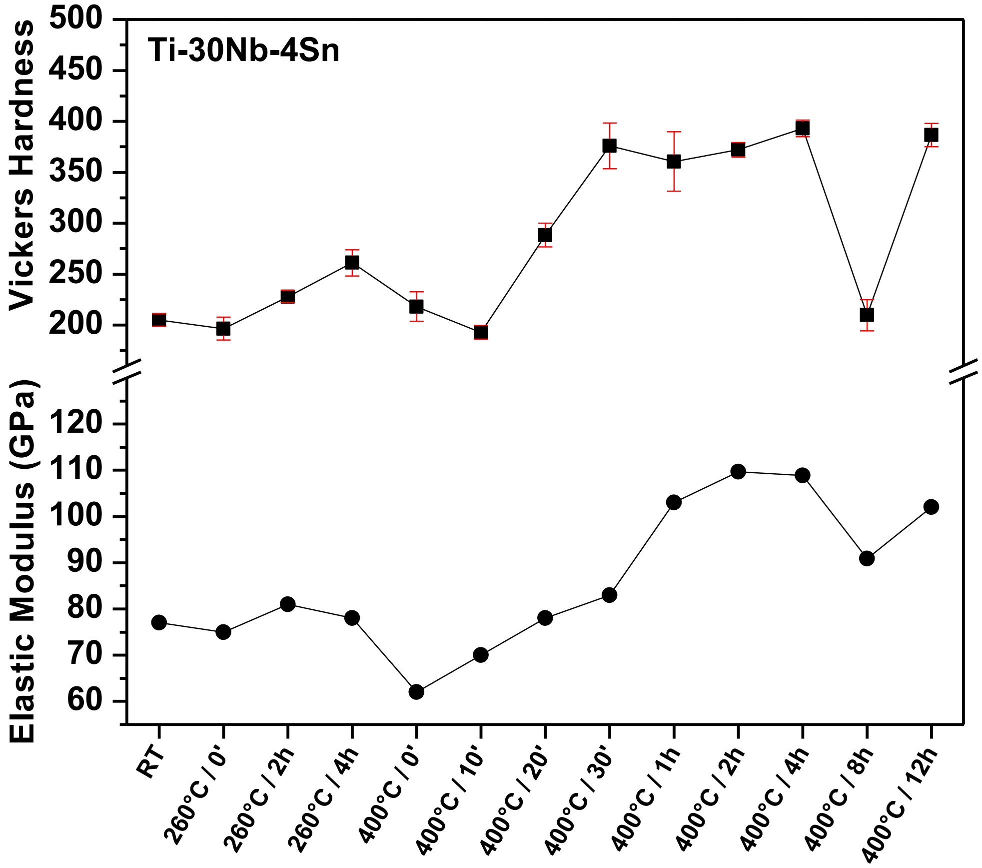
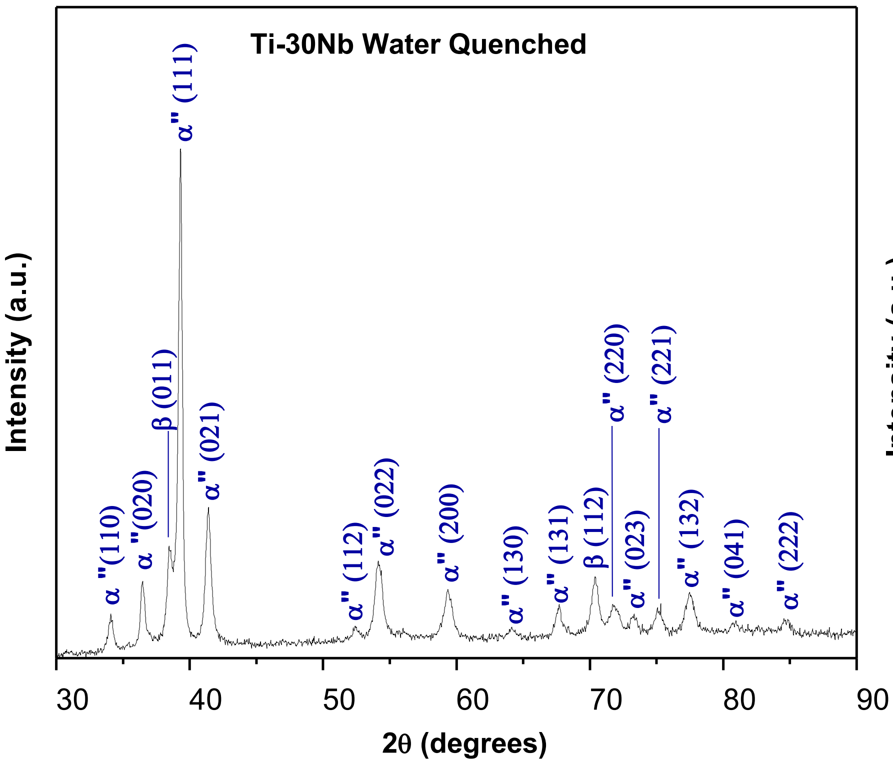
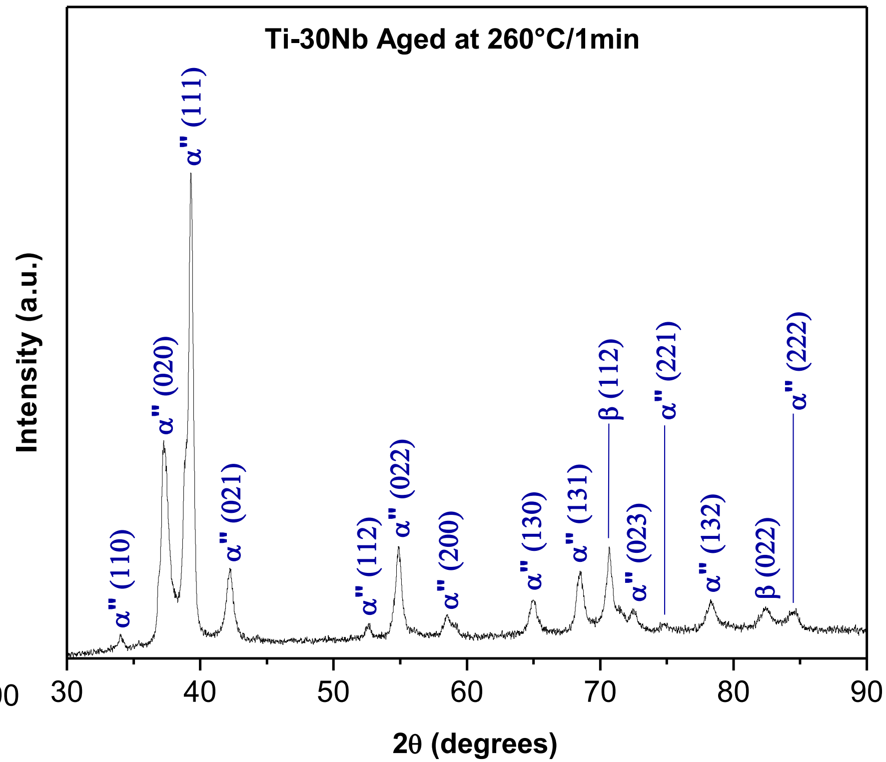


Elastic Modulus and Hardness



XRD Patterns





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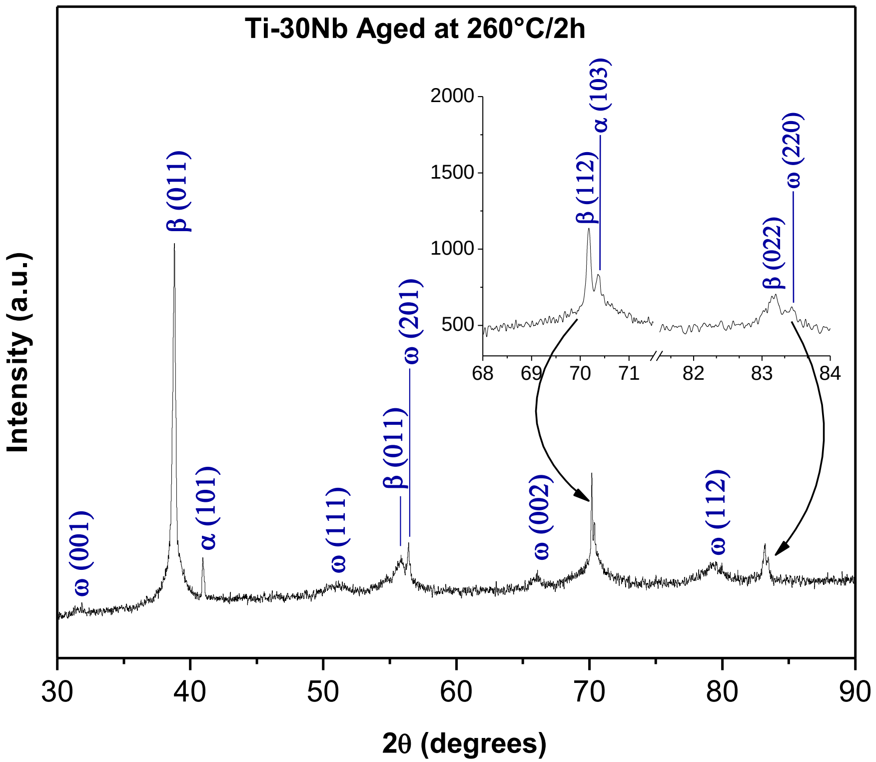

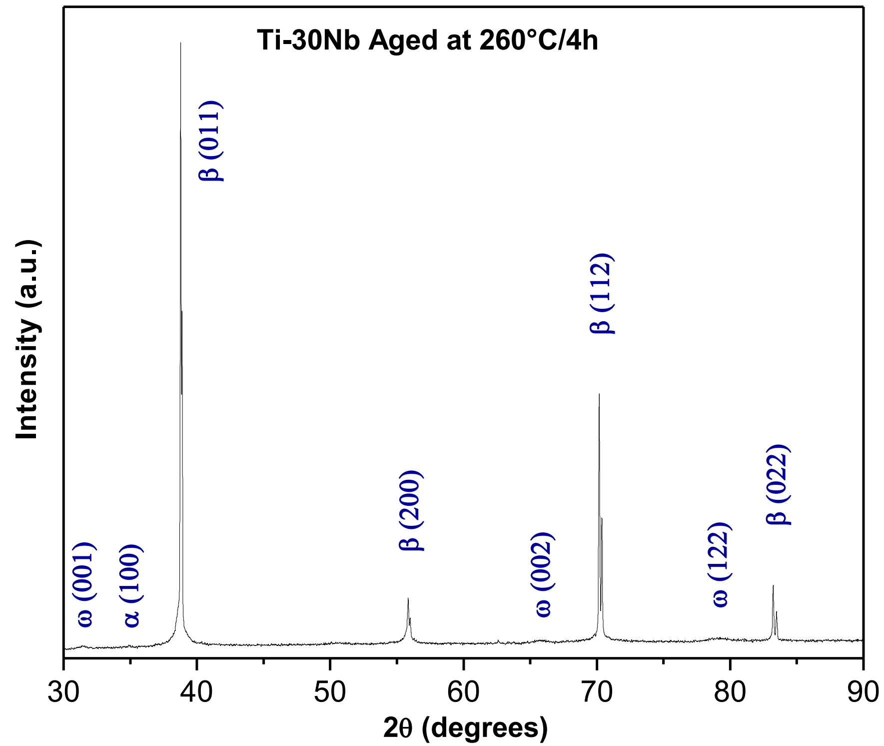

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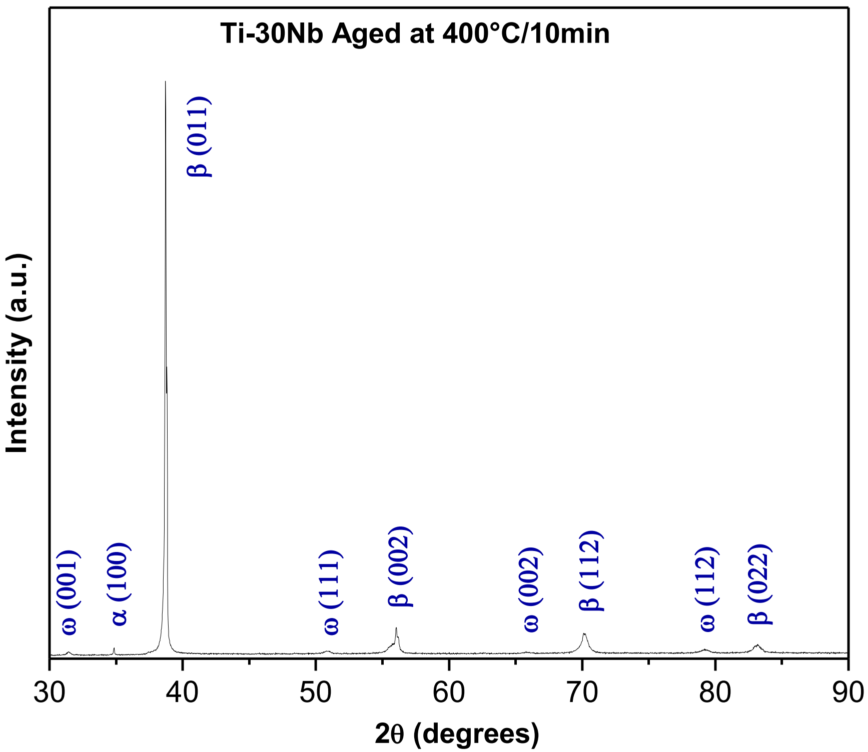

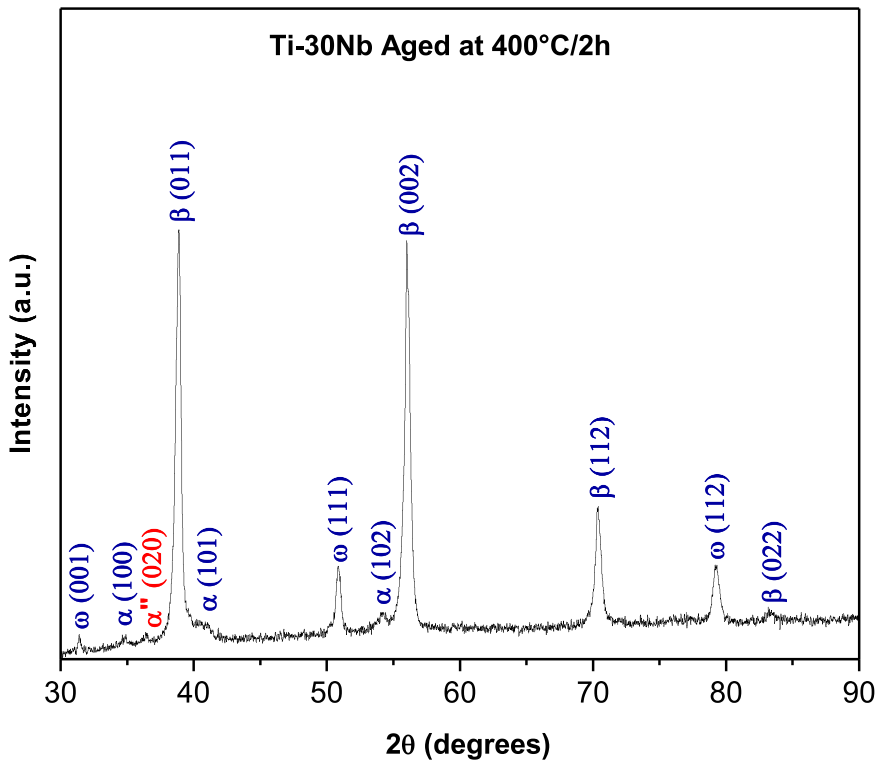

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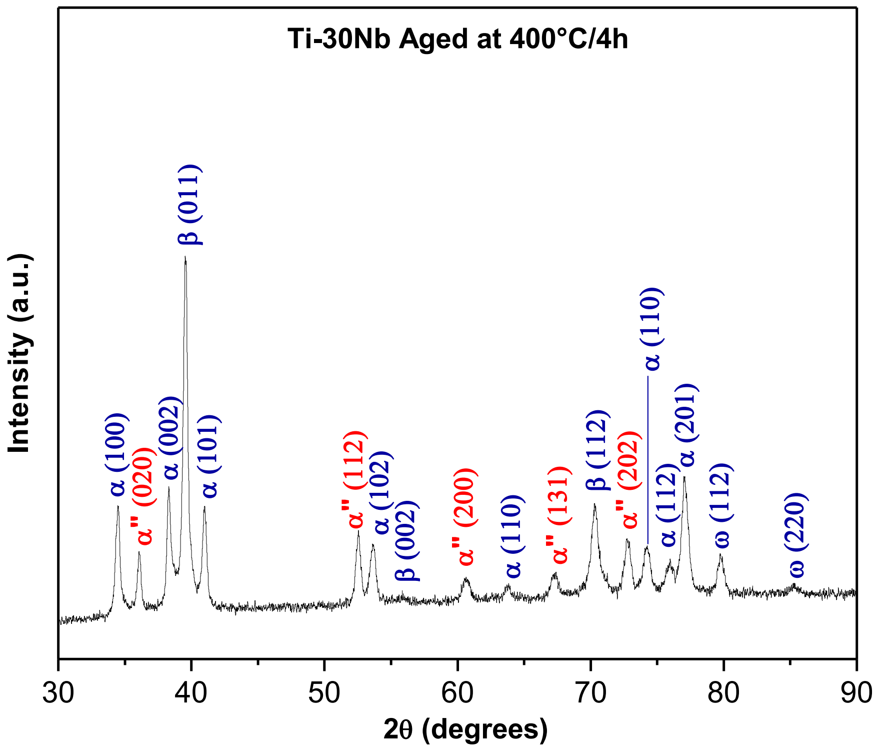
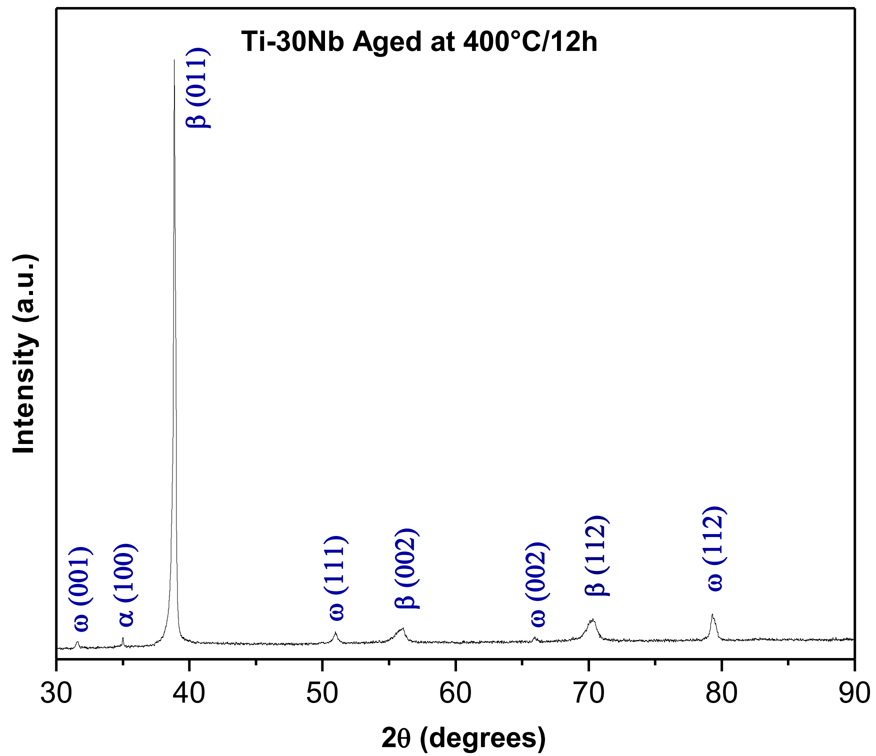
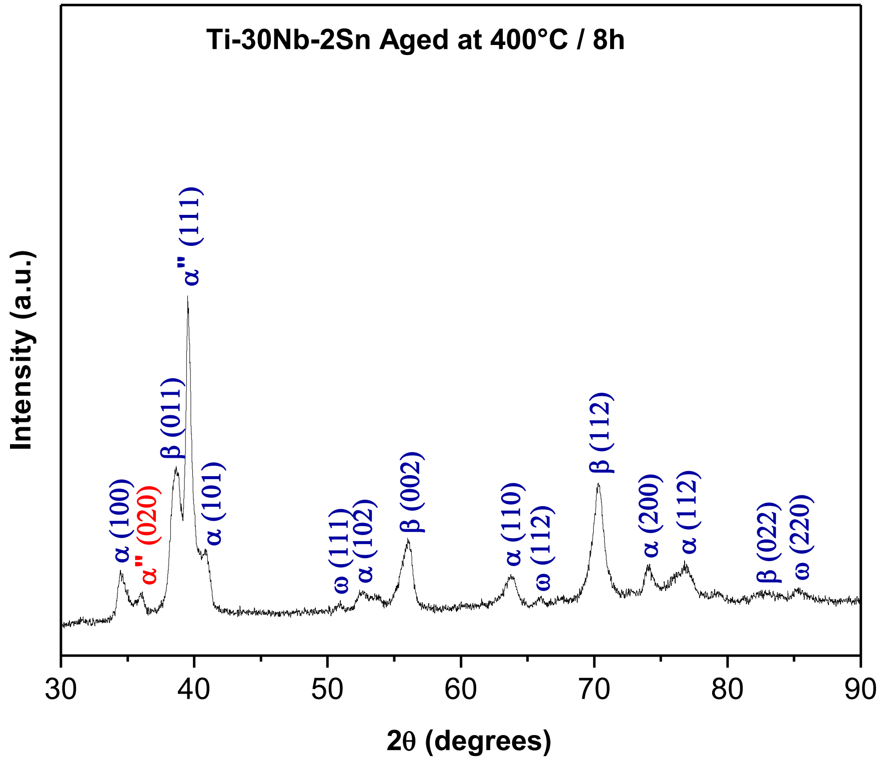
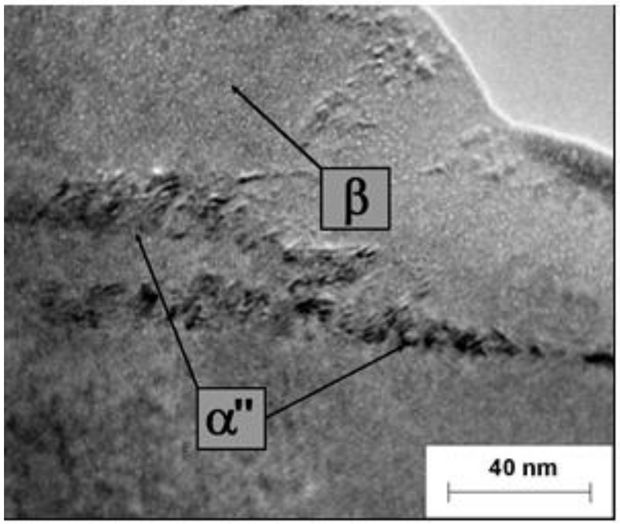




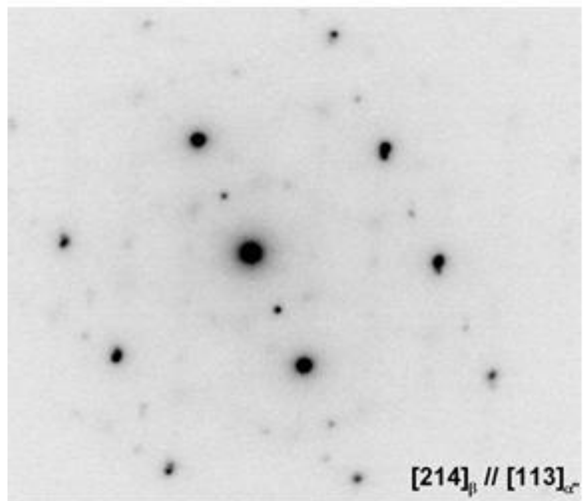
XRD Patterns



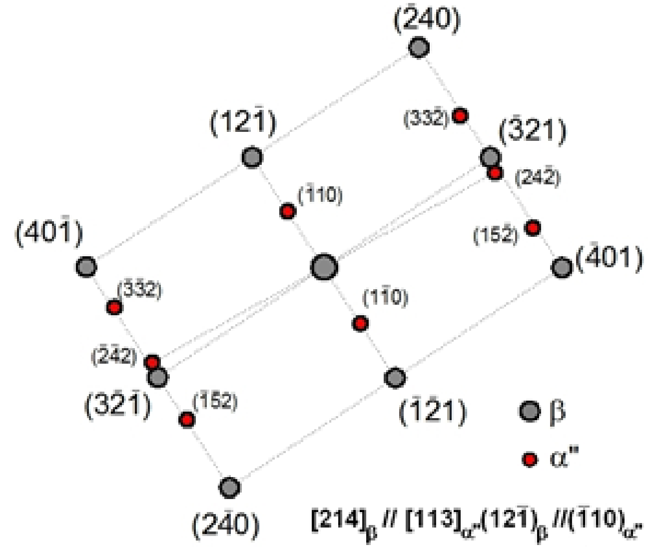
TEM - Ti-30Nb aged at 400ºC/4 h



HRTEM image showing α” in β matrix



SADP: [214]β zone axis and [113] α” zone axis



Indexed SADP

Orthorhombic Symmetry Phase

- **Intriguing observation: formation of orthorhombic symmetry phase during the aging of Ti-30Nb (400 ^{o}C/4 h).**
- **Ti-30Nb-2Sn alloys also showed precipitation of orthorhombic phase during aging heat treatment**
- **Ti-30Nb-4Sn does not seem to show precipitation of orthorhombic phase during aging heat treatment**
- **How was this orthorhombic phase formed?**
  - **Transition phase in metastable β decomposition?**
  - **Induced by air cooling?**

Transition Phase

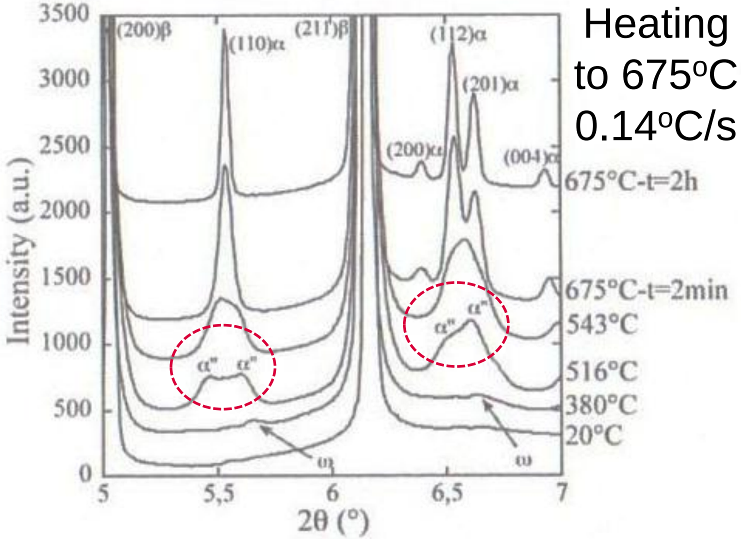
- **Orthorhombic phase formation may be a transition phase which occurs during the decomposition of metastable β phase, and over certain composition range(s)**

Transition Metastable Phase

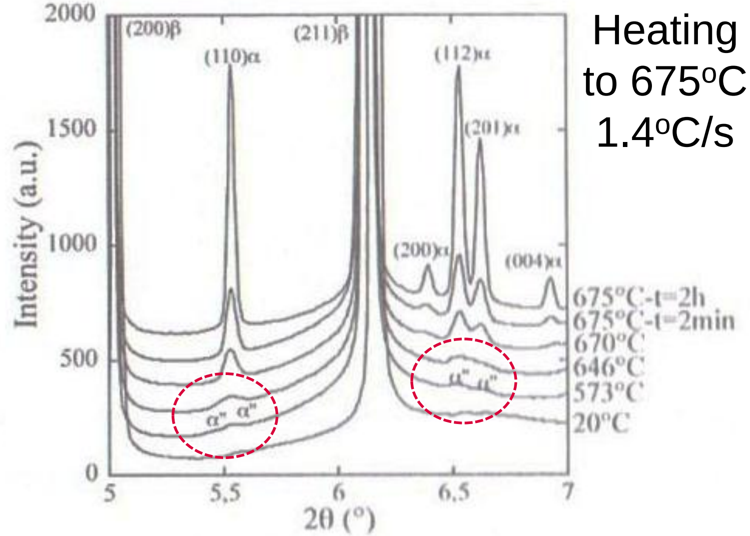
- **Decomposition of β metastable on aging in Ti-5553 alloy**
- **Depending on heating rates, three transformation sequences were found:**
  - **0.1^{o}C/s:** $\beta \rightarrow \beta + \omega_{iso} \rightarrow \beta + \alpha'' + \alpha \rightarrow \beta + \alpha$
  - **1^{o}C/s:** $\beta \rightarrow \beta + \alpha'' \rightarrow \beta + \alpha'' + \alpha \rightarrow \beta + \alpha$
  - **Higher heating rate:** $\beta \rightarrow \beta + \alpha$

  - **A. Settefrati et al., Solid State Phenomena 173 (2011) 760**

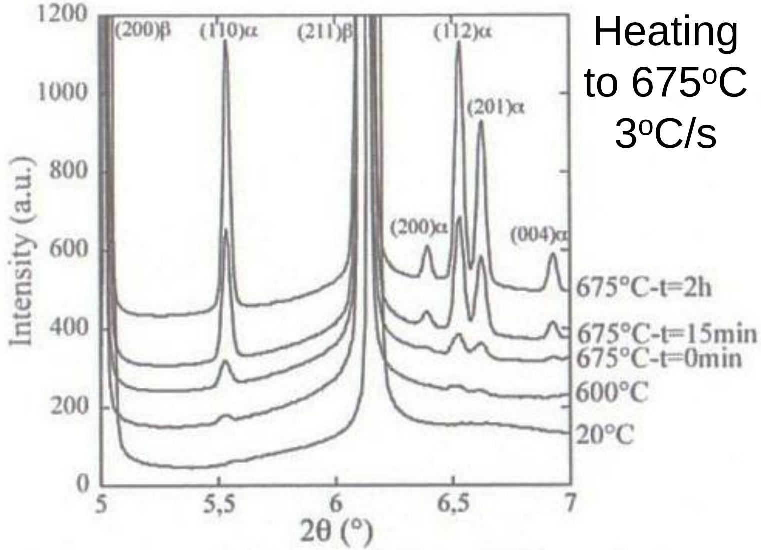
Heating to 675°C 0.14°C/s



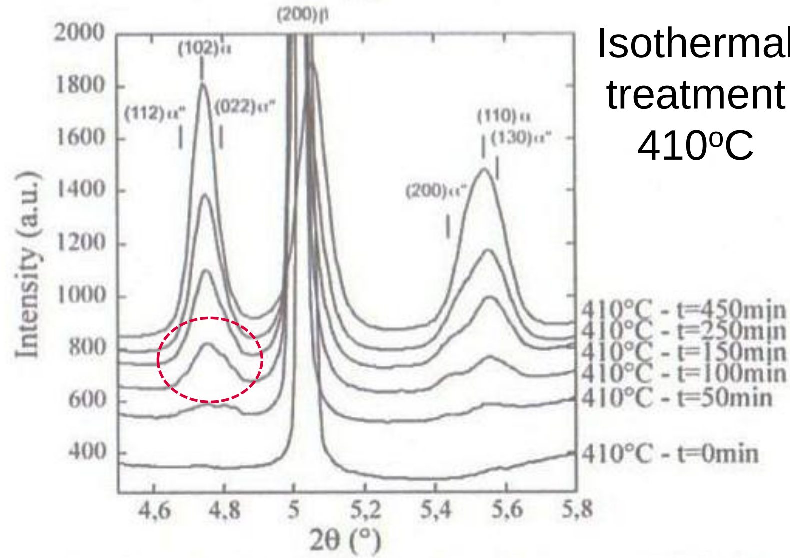
Heating to 675°C 1.4°C/s



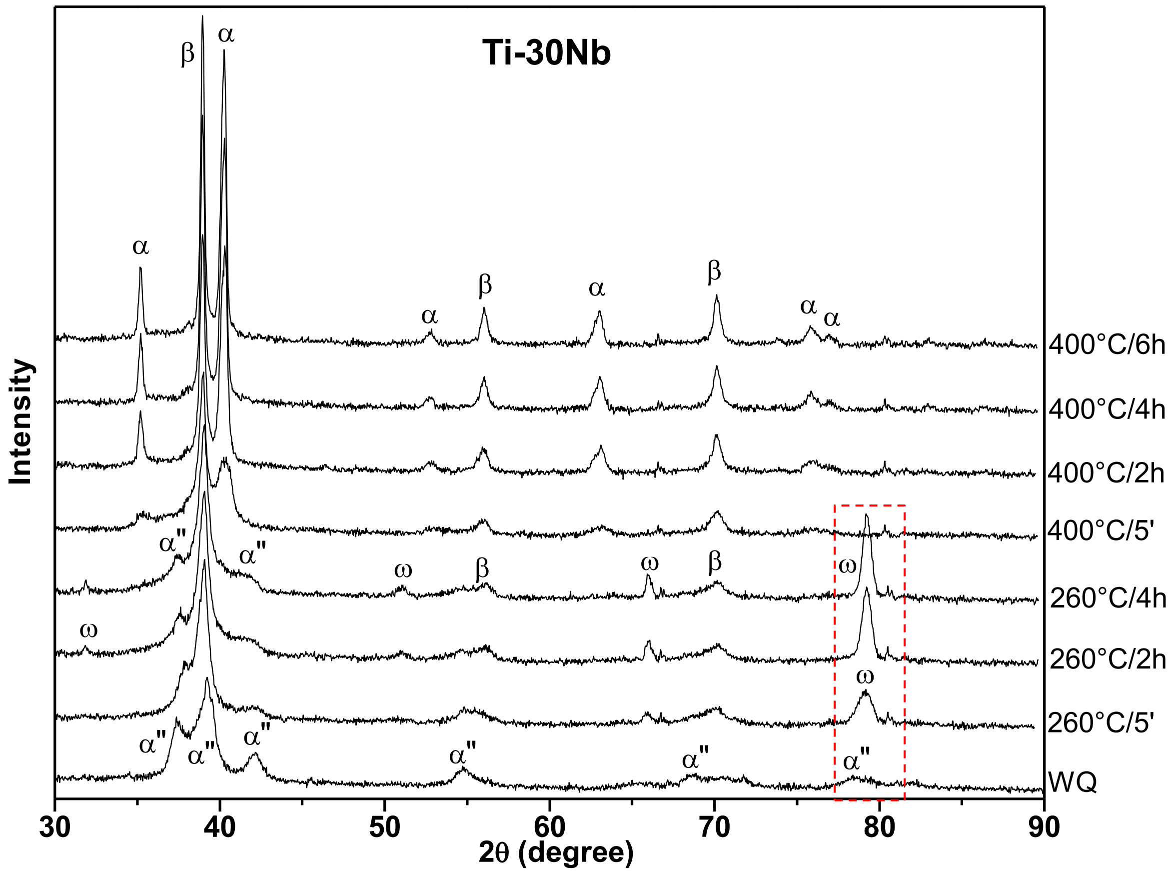
Heating to 675°C 3°C/s



Isothermal treatment 410°C

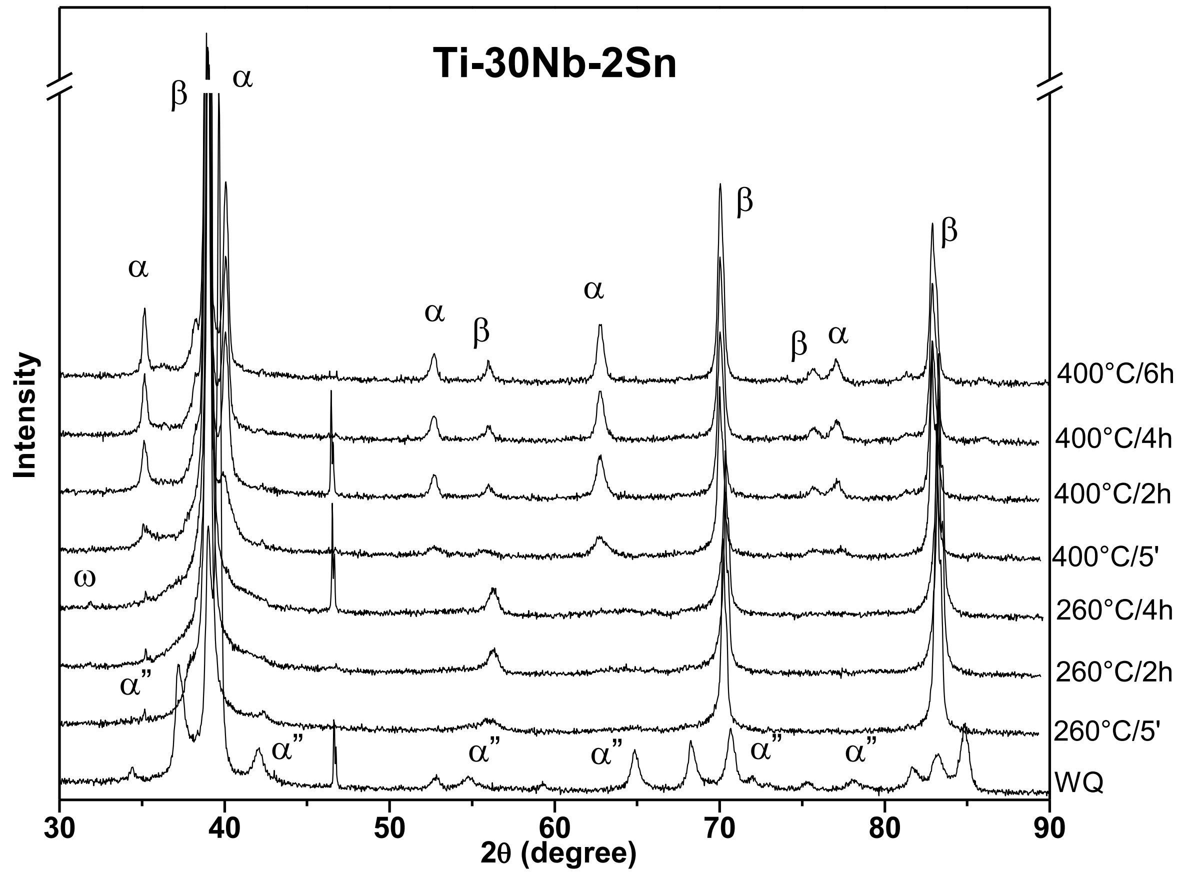


HTXRD

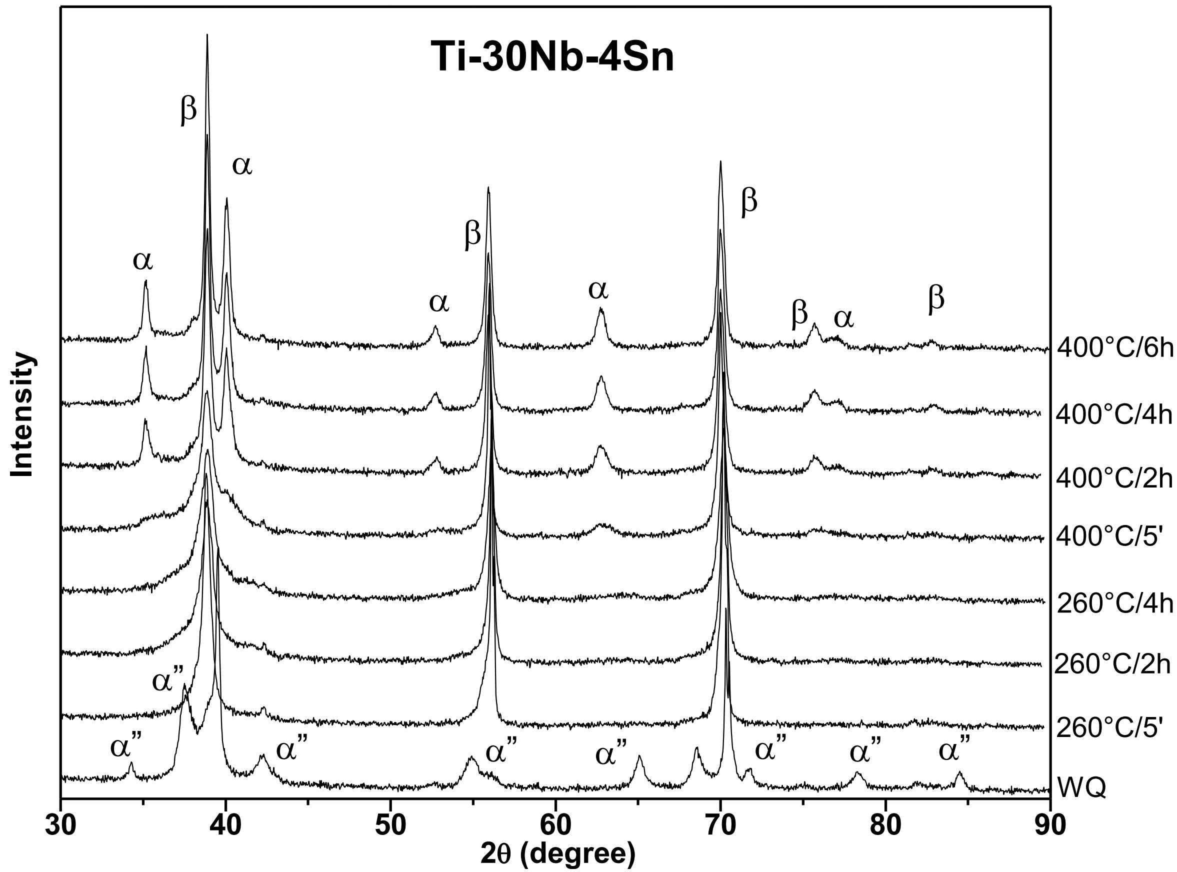


Ti-30Nb
Intensity
2θ (degree)
30
40
50
60
70
80
90
400°C/6h
400°C/4h
400°C/2h
400°C/5'
260°C/4h
260°C/2h
260°C/5'
WQ
α
β
ω
α"

HTXRD

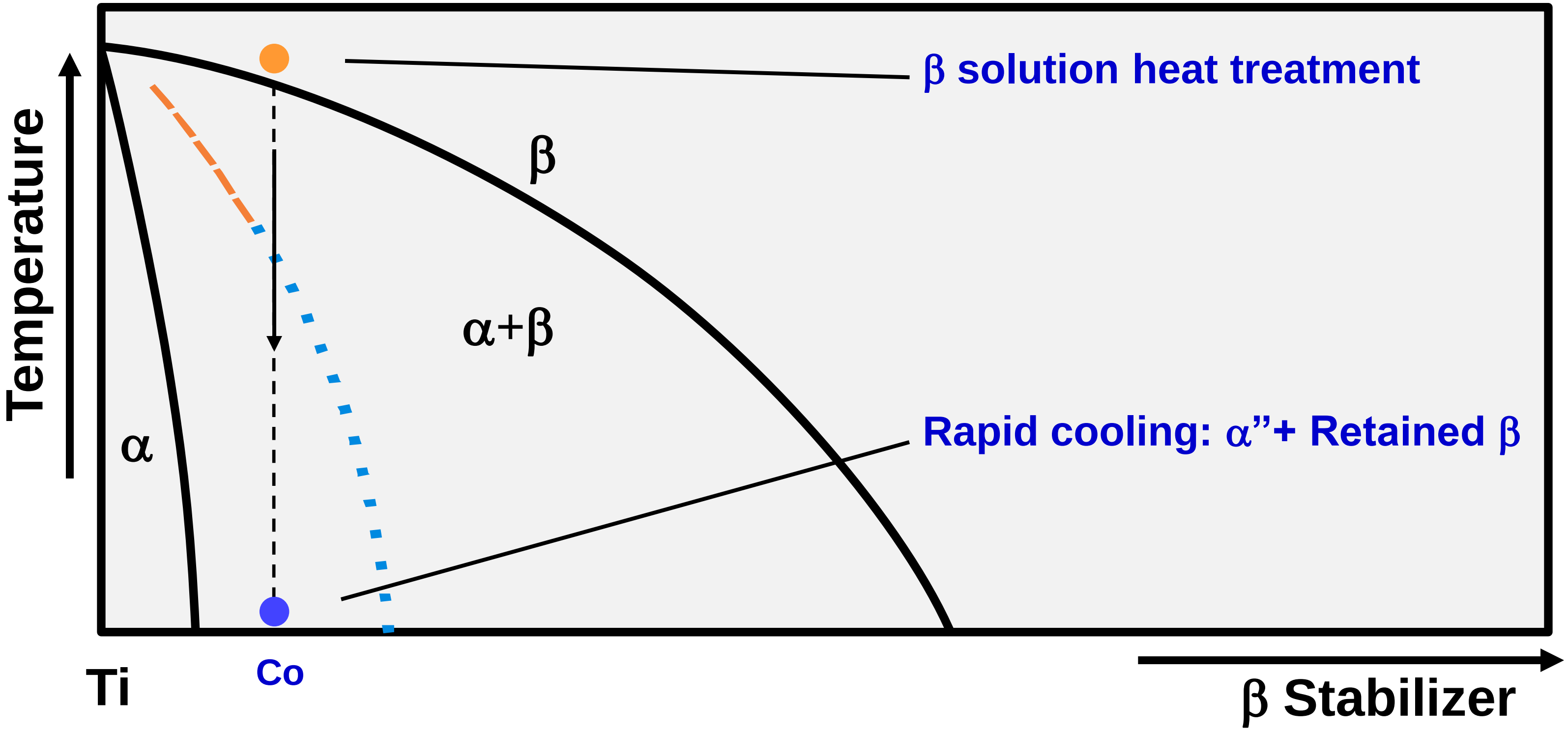

Ti-30Nb-2Sn
Intensity
2θ (degree)
30
40
50
60
70
80
90
α
β
α
α
β
α
β
β
β
α
ω
α”
α”
α”
α”
α”
α”
400°C/6h
400°C/4h
400°C/2h
400°C/5'
260°C/4h
260°C/2h
260°C/5'
WQ

HTXRD

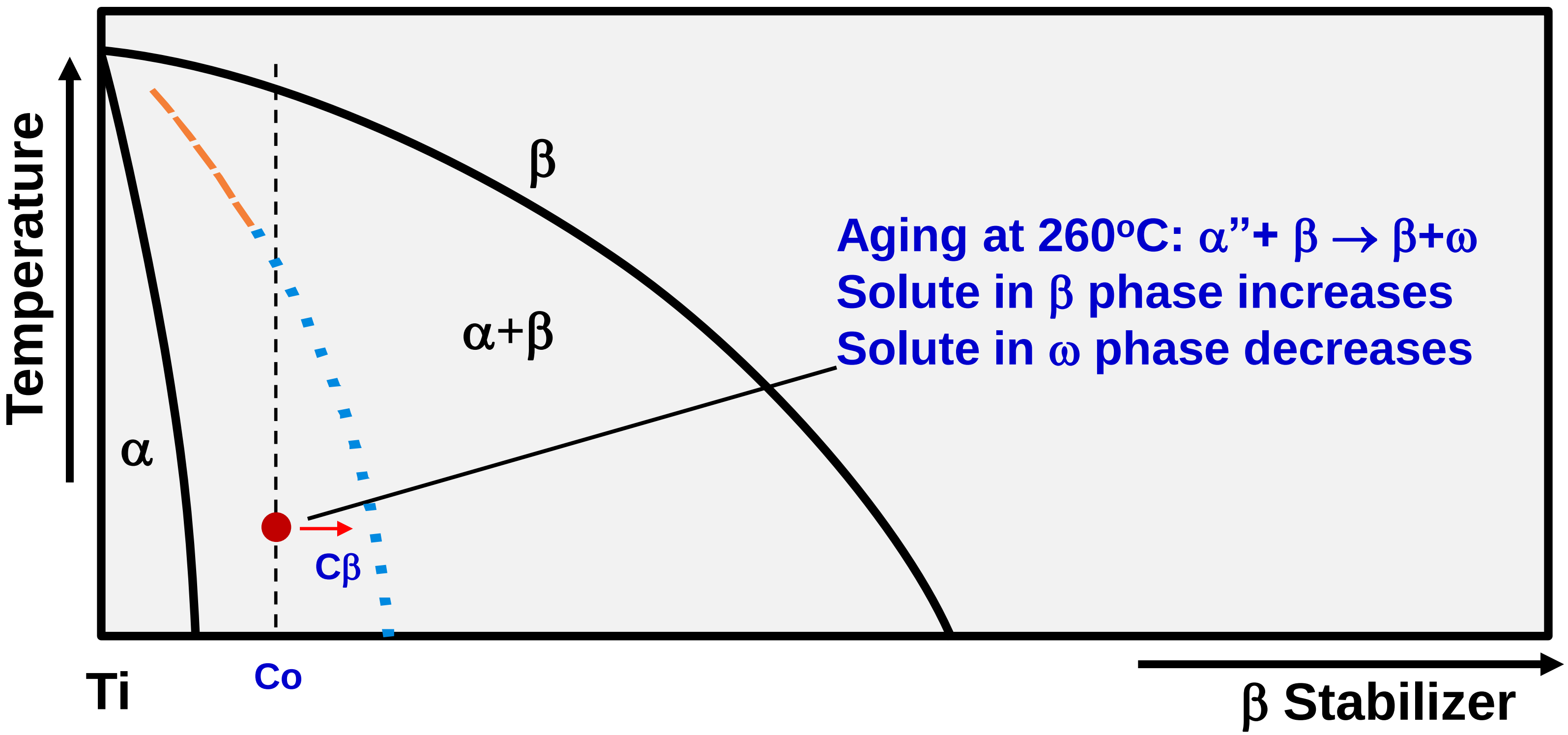


Ti-30Nb-4Sn
Intensity
2θ (degree)
30
40
50
60
70
80
90
β
α
α
β
α
β
α
β
α
β
α''
α''
α''
α''
α''
α''
α''
α''
400°C/6h
400°C/4h
400°C/2h
400°C/5'
260°C/4h
260°C/2h
260°C/5'
WQ

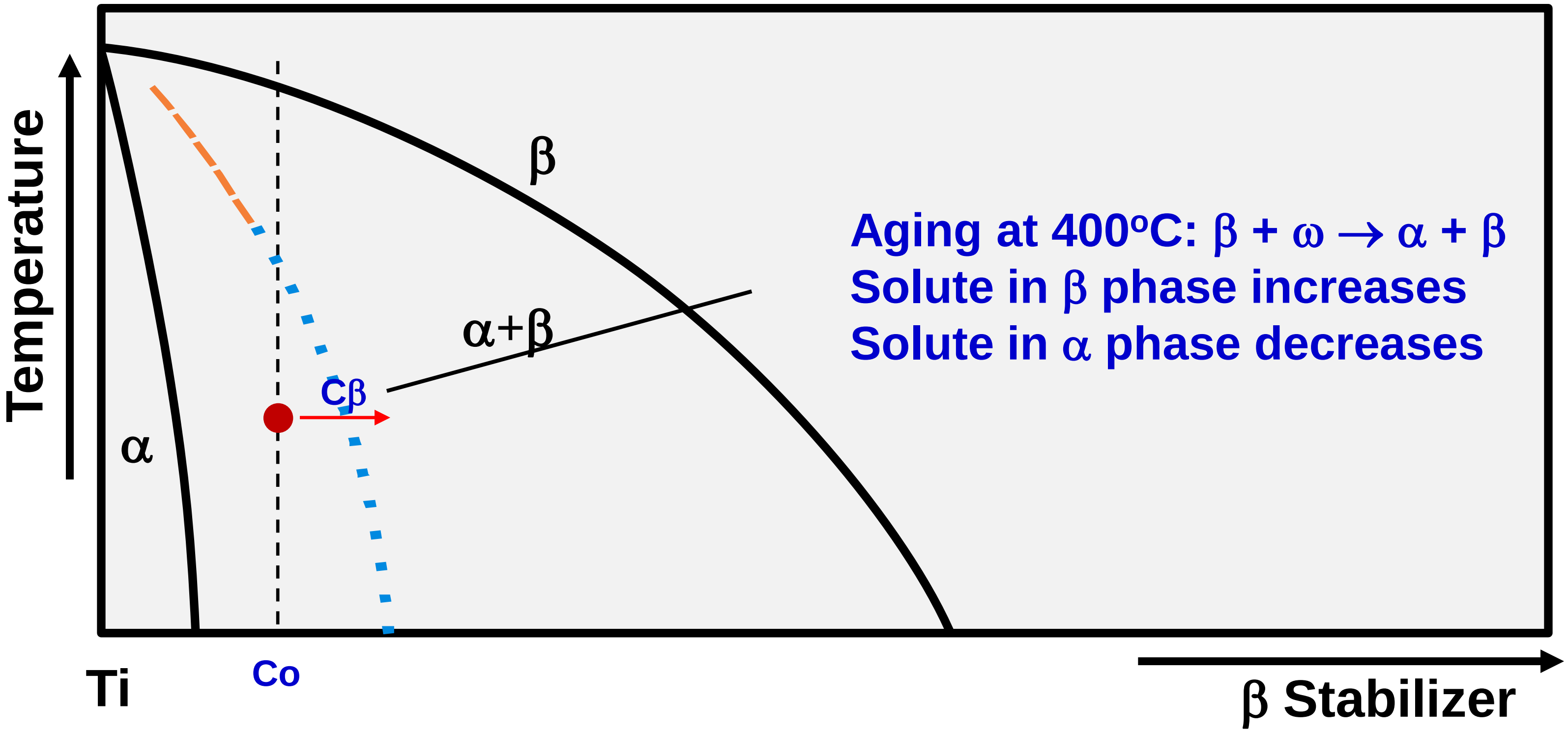
Induced by Air Cooling



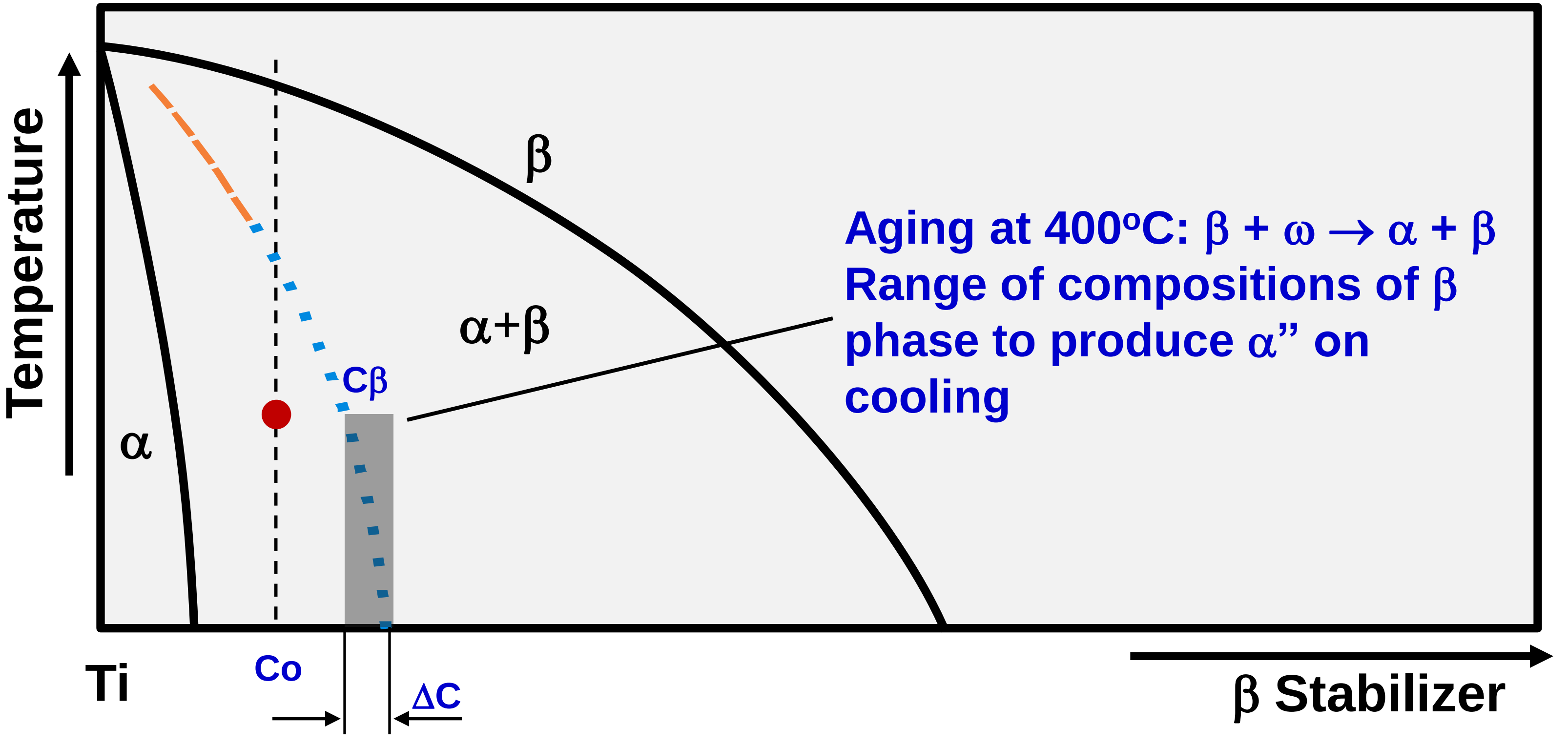
Induced by Air Cooling



Induced by Air Cooling



Induced by Air Cooling



Mechanical Behavior

Alloy Condition	Phases (XRD)	σ_{UTS} (MPa)	Elong (%)	E (GPa)	Hardness (VH)
Ti-30Nb WQ	$\beta+\alpha''+\omega$	532 ± 21	30 ± 7	74	199 ± 6
Ti-30Nb Aged	$\beta+\alpha+\omega$	846 ± 24	0.8 ± 0.1	105	424 ± 10
Ti-30Nb-2Sn WQ	$\beta+\alpha''$	500 ± 32	36 ± 4.0	70	219 ± 5
Ti-30Nb-2Sn Aged	$\beta+\alpha+\omega$*	857 ± 22	0.8 ± 0.2	100	432 ± 15
Ti-30Nb-4Sn WQ	$\beta+\alpha''$	531 ± 20	21.6 ± 1.2	62	211 ± 7
Ti-30Nb-4Sn Aged	$\beta+\alpha+\omega$**	850 ± 18	1.2 ± 4.3	101	387 ± 11

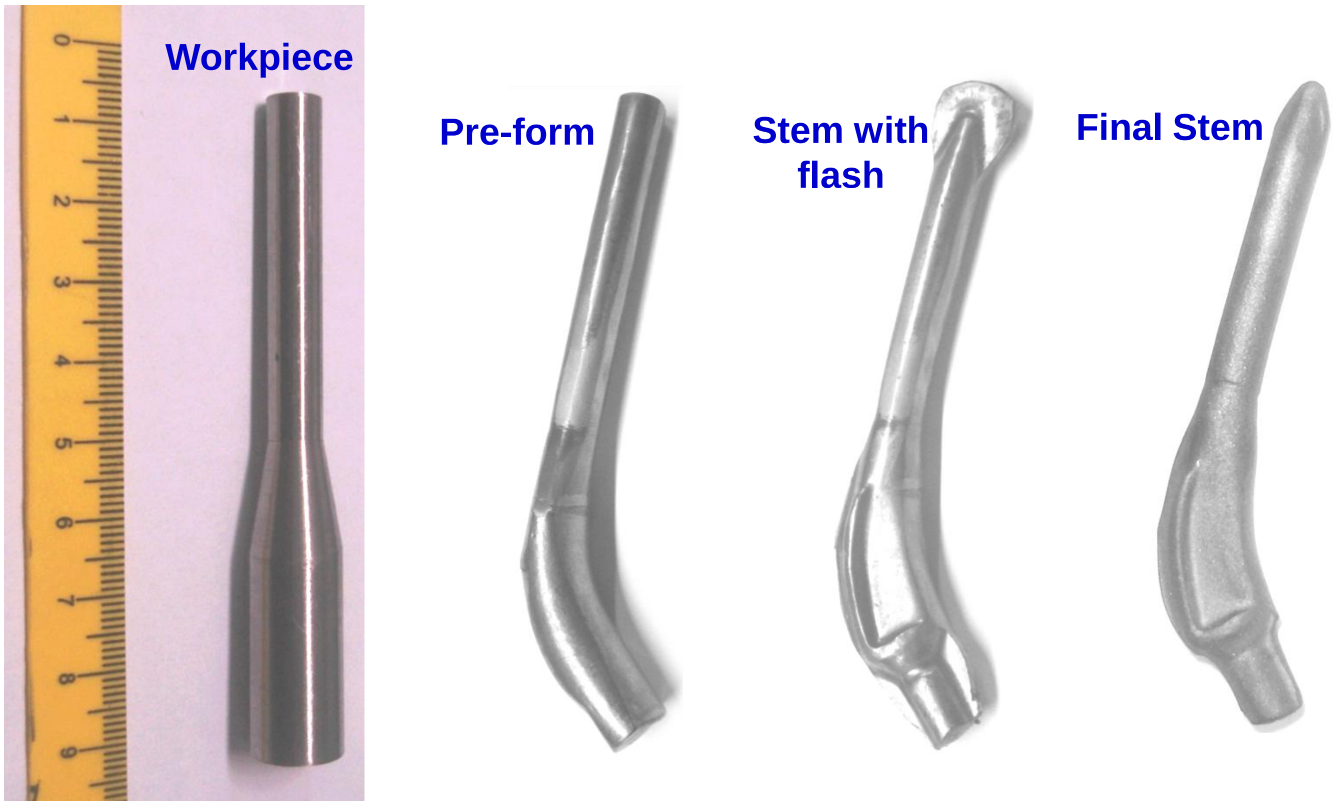
ω* - small amount **ω** - very small amount**

Possible Applications of Ti-Nb-Sn Alloys

Femoral Stem Forging

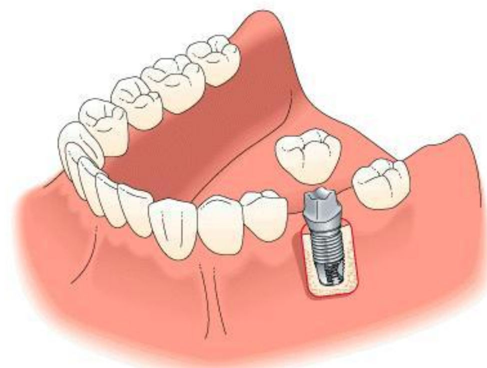
- **Femoral stem produced by hot forging**
- **T above 1000ºC**
- **Alpha-case**
- **Oxidization**
- **Die degradation**

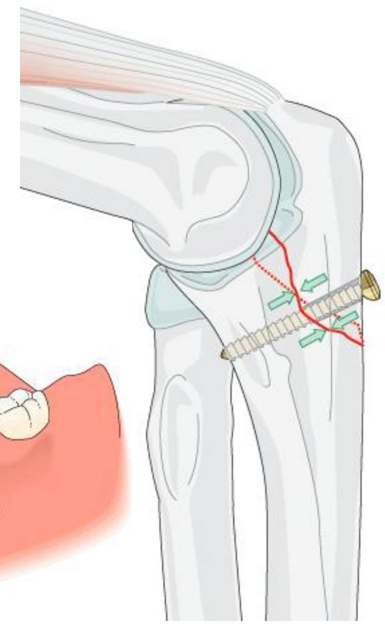
Cold Forging



Screw for Implants

- **Screws are made using Ti Alloys**
- **Screws are used in dental and orthopedic implants**





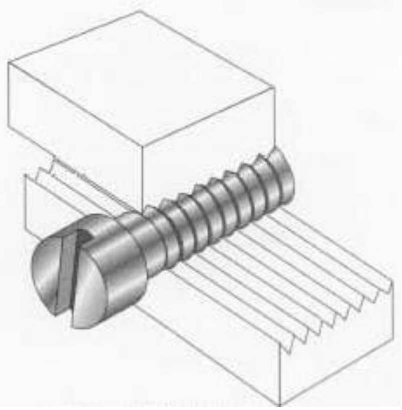
Screw for Implants

- **Usually, Ti alloys screws for implants are manufactured by machining because plastic deformation is challenging**
- **Ti Alloys: High yield strength and low elastic modulus = spring back phenomenon**

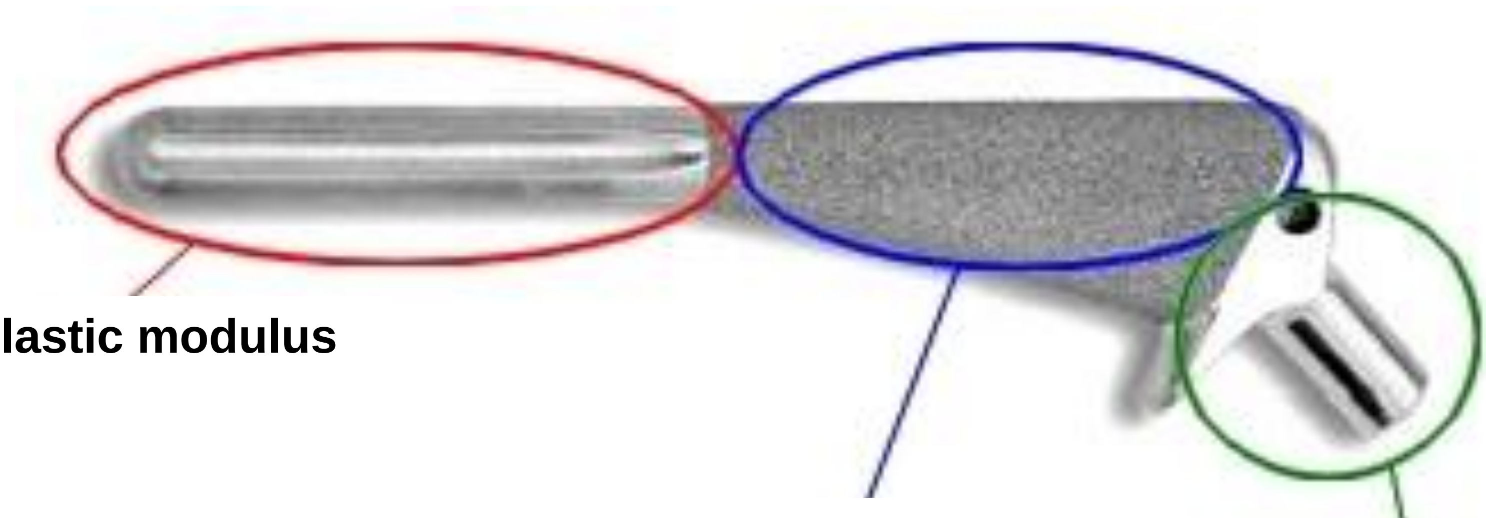
Screw for Implants

- **WQ Ti-Nb-Sn alloys with low yield strength allow one to use more conventional screw manufacturing processes:**

Cross rolling



Hybrid Mechanical Behavior

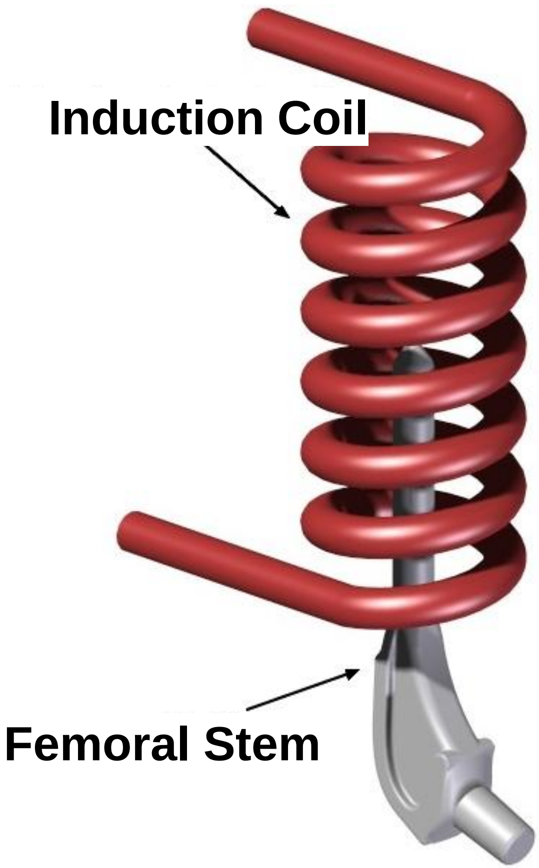


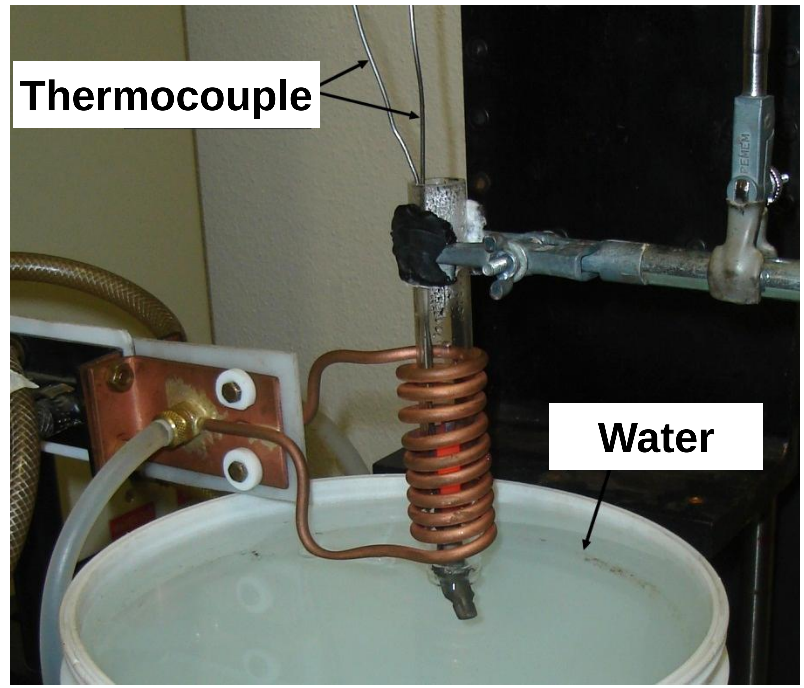
Low elastic modulus

High Fatigue Strength
High Yield strength

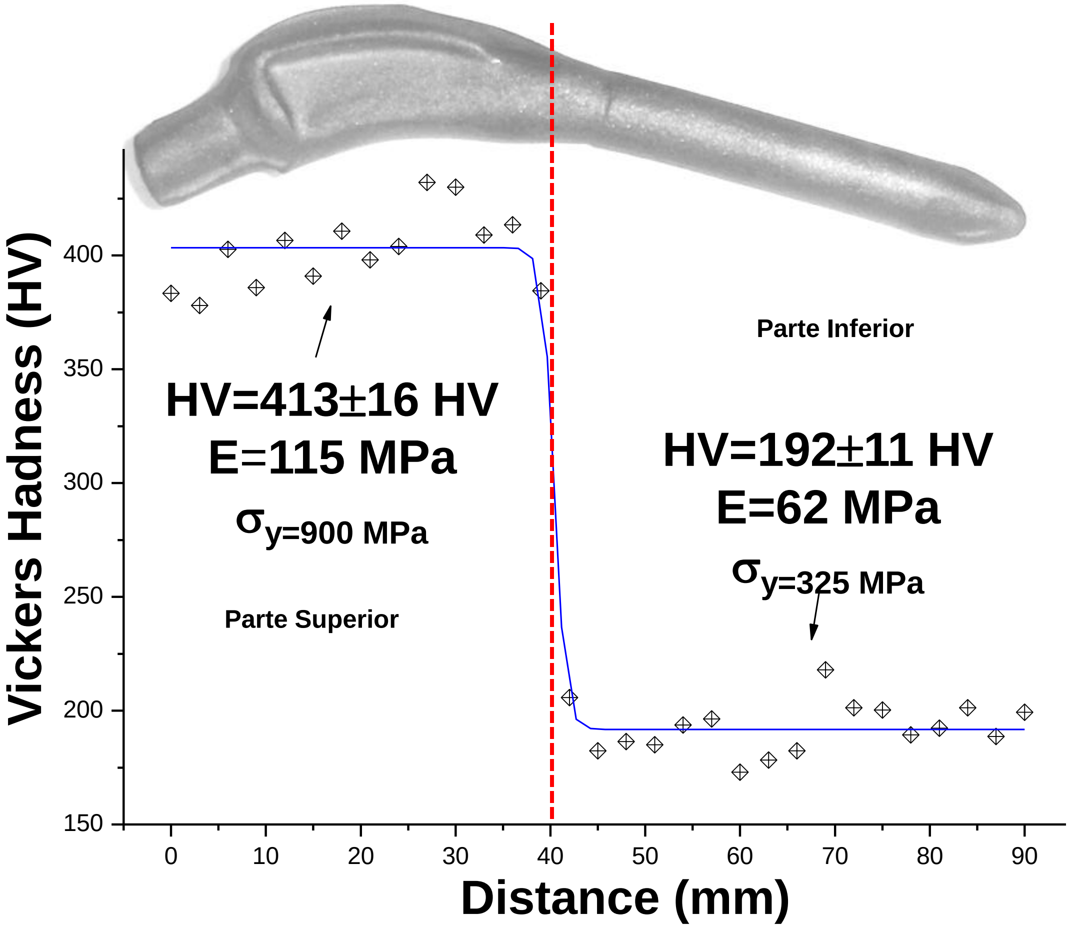
High Fatigue Strength
High Yield strength
High Corrosion Resistance

Selective Heat Treatment





Hybrid Mechanical Behavior



Conclusions

- WQ Ti-30Nb, Ti-30Nb-2Sn and Ti-30Nb-4Sn alloys showed β and α" and the amount of α" decreases with addition of Sn;
- α" decomposition results in precipitation of β, ω and α phases;
- Sn may act as a suppressor of ω phase precipitation;
- Orthorhombic symmetry phase formation not completely understood and more work (TEM and HTXRD) is needed to find its origin;
- (1h/1000ºC/WQ) samples showed yield strength below 310 MPa (easy cold forging) - aged sample value increased up to 850 MPa
- (1h/1000ºC/WQ) samples showed elastic modulus below 62 GPa
- Finally, besides stable phases, controlled precipitation of metastable phases is of paramount importance when designing Ti alloys for orthopedic applications

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- **Questions?**