Titanium and titanium alloys

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Lecture 2: Fundamentals of Ti alloys

- Polymorphism
  - Alpha phase
  - Beta phase
- Pure titanium
- Titanium alloys
  - $\alpha$ alloys
  - $\alpha + \beta$ alloys
  - $\beta$ alloys
- Phase transformation $\beta \rightarrow \alpha$
- $\omega$–phase
- Hardening mechanisms in Ti
  - Hardening of $\alpha + \beta$ alloys
  - Hardening of metastable $\beta$ alloys
Polymorphism

• Pure titanium is polymorphic – it exists in more crystallographic structures (phases)
  • Similarly to iron

• Above 882°C the titanium is body-centered cubic material (bcc) – β – phase

• Upon cooling below 882°C – (so-called β–transus temperature) – β – phase martensitically transforms to hexagonal close-packed structure - α – phase
Stable phases – pure titanium

- **β** – phase – stable above 882°C (β–transus temperature)
- Under room temperature, only **α** – phase is stable

Hexagonal close-packed lattice (hcp)
Phase **α**

Body-centered cubic lattice (bcc)
Phase **β**

6 atoms / 0.106 μm³ = **56,6**

2 atoms / 0.0366 μm³ = **54,6**

This difference allows dilatometry studies.
HCP – hexagonal closed packed

α – phase

Plane - \( (hkl) \)
Set of planes - \{hkl\}
Direction - \([UVW]\)
Set of directions – \(<UVW>\)

c/a(Ti) = 1.588 < 1.633 (optimal)
c/a(Cd) = 1.886
c/a(Zn) = 1.856
c/a(Mg) = 1.624
c/a(Co) = 1.623
c/a(Zr) = 1.593

Slip systems:
Principal: Prismatic \{1 0 -1 0\} \(<1 1 -2 0>\)
Secondary: Basal \{0 0 0 1\} \(<1 1 -1 0>\)
Other:
Pyramidal \{1 0 -1 1\} \(<1 1 -2 0>\) and \{1 1 -2 2\} \(<1 1 -2 3>\)
HCP – hexagonal closed packed

Slip systems
Principal: Prismatic \{1\ 0\ -1\ 0\} <1\ 1\ -2\ 0>  
Secondary: Basal \{0\ 0\ 0\ 1\} <1\ 1\ -1\ 0>  
Other:
Pyramidal \{1\ 0\ -1\ 1\} <1\ 1\ -2\ 0> and  
\{1\ 1\ -2\ 2\} <1\ 1\ -2\ 3>  

![Basal Slip System](image1)

Basal-<\mathbf{a}>  
(0001) <1120>, 3  

![Prismatic Slip System](image2)

Prismatic-<\mathbf{a}>  
\{10\bar{1}0\} <11\bar{2}0>, 3  

![Pyramidal Slip System](image3)

Pyramidal-<\mathbf{a}>  
\{10\bar{1}1\} <11\bar{2}0>, 6  

![1st Order Pyramidal Slip System](image4)

1st order Pyramidal-<\mathbf{c} + \mathbf{a}>  
\{10\bar{1}1\} <11\bar{2}3>, 12  

![2nd Order Pyramidal Slip System](image5)

2nd order Pyramidal-<\mathbf{c} + \mathbf{a}>  
\{11\bar{2}2\} <11\bar{2}3>, 6
The effect of alloying elements on phase composition

• Alloying elements affect the beta-transus temperature
• $\alpha$ – stabilizing elements – increase beta-transus temperature
• $\beta$ – stabilizing elements – increase beta-transus temperature
  – Isomorphous – completely soluble in solid solution
  – Eutectoid – intermetallic particles are created
The effect of alloying elements on phase composition

- Neutral elements – \( \text{Zr, Sn} \)
- \( \alpha \) - stabilizing elements – \( \text{Al, O, N, C} \)
- \( \beta \) - stabilizing elements – isomorphous – \( \text{Mo, V, Ta, Nb} \)
- \( \beta \) - stabilizing elements – eutectoid – \( \text{Fe, Mn, Cr, Co, Ni, Cu, H} \)
Titanium alloys

• Pure Ti at room temperature $\rightarrow$ only $\alpha$ – phase
• Low-content of $\beta$-stabilizing elements (and/or outweighed by $\alpha$ -stabilizing elements) $\rightarrow$ only $\alpha$ – phase is stable at RT $\rightarrow$ so-called $\alpha$ – alloys

• Increased content of $\beta$-stabilizing elements
  • $\beta$ – phase becomes stable at room-temperature
  • $\alpha + \beta$ alloys
Titanium alloys

- Further increased content of $\beta$-stabilizing elements
  - The temperature „martenzite start“ of phase transition $\beta \rightarrow \alpha$ is decreased below room temperature
  - Phase $\alpha$ is not formed during quenching
  - **Metastable $\beta$-alloys**
  - During annealing below $\beta$-transus temperature, the $\alpha$ phase is created until the balance composition is achieved
Titanium alloys

- Even more increased content of $\beta$-stabilizing elements
  - Beta transus temperature can be decreased below RT
  - After cooling to room temperature, $\beta$ phase remain stable
  - Stable $\beta$-alloys
Molybdenum equivalence

• Mo: one of the most important $\beta$ – stabilizing elements
• Comparison of $\beta$– stabilizing effect of different elements
  → so-called molybdenum equivalence
• $[\text{Mo}]_{eq} = [\text{Mo}] + 0,67 [\text{V}] + 0,44 [\text{W}] + 0,28 [\text{Nb}] + 0,22 [\text{Ta}] +$
  $+ 2,9 [\text{Fe}] + 1,6 [\text{Cr}] + 1,25 [\text{Ni}] + 1,7 [\text{Mn}] + 1,7 [\text{Co}] - 1,0 [\text{Al}]$
• i.e. Vanadium content must be 1.5 times higher then Molybdenum to achieve the same effect on stability of beta phase
• i.e. Iron is three times stronger beta stabilizer than Mo a 4x than V
• Molybdenum equivalence is only empirical rule based on analysis of binary alloys
• Molybdenum equivalence cannot be used quantitatively to compute beta transus temperature or equilibrium phase composition
  – Especially in the case of ternary and more complicated alloys
Aluminium equivalence

• Less used analogy of molybdenum equivalence for α - stabilizers

• Al: one of the most important α – stabilizing elements

\[ \text{[Al]}_{\text{eq}} = \text{[Al]} + 0.33 \text{[Sn]} + 0.17 \text{[Zr]} + 10 \text{[O + C +2N]} \]

• In the case that Al equivalence is higher than approx 9% (some sources say 5%), then Ti₃X intermetallic particles are formed

• The effect of Zr remains unknown and depends strongly on the content of other alloying elements
Phase transformation $\beta \rightarrow \alpha$

- Occurs below $\beta$-transus temperature
- In pure Ti, $\alpha$-alloys and $\alpha + \beta$ alloys
  - $\rightarrow$ martensitic transformation
  - But not until equilibrium phase composition
  - Followed by growth of particles (lamellae)

- In metastable $\beta$–alloys
  - Precipitation of $\alpha$–particles
    - Homogeneous precipitation
    - Heterogeneous precipitation
      - Grain boundaries
      - Particles of other phases
      - Chemical inhomogeneities
Phase transformations in metastable β alloys

1. Phase separation: $\beta \rightarrow \beta_{\text{lean}} + \beta_{\text{rich}}$ také $\beta \rightarrow \beta' + \beta$
   - Occurs in strongly stabilized β-alloys
   - β-stabilization elements form clusters via spinodal decomposition $\rightarrow \beta_{\text{rich}}$ regions

2. Formation of $\omega$–phase
   - Less stabilized β-alloys
   - Formation of particles $\omega$
   - Small coherent particles, size: 1-20 nm

3. Precipitation of $\alpha$–phase from $\omega$–phase
   - Small $\omega$ phase particles serve as precursors of $\alpha$ phase precipitation
     $\rightarrow$ precipitates of $\alpha$ phase are tiny and homogeneously distributed
     $\rightarrow$ significant strengthening
ω-phase

- Hexagonal (but not hcp) phase
- Nanometer sized particles
- Created after quenching (ω-athermal)
- Grow during ageing

Transmission electron microscopy

Devaraj et al., Acta Mat 2012
Ti-9Mo
a,b) – quenched from β;
c)-e) – 475°C/30 mins;
f)-h) - 475°C/48 h
β → ω → α phase transformations

- Volume fraction of phases in Ti-LCB alloy studied by X-ray diffraction
- β + ω transforms to α with increasing ageing temperature and ageing time (isothermal annealing)

Ageing at 400°C

Ageing at 450°C

Smilauerova et al., unpublished research
\[ \beta \rightarrow \omega \rightarrow \alpha \] phase transformations

- Identified by in-situ methods
  - Differential scanning calorimetry
  - Measurements of electrical resistivity
- \[ \beta \rightarrow \omega \rightarrow \alpha \] transformations identified during heating 5°C/min

I. Dissolution of athermal \( \omega \) phase, reversible diffusionless process
II. Stabilization and growth of isothermal \( \omega \) phase – diffuse process
III. Dissolution of \( \omega \) phase
IV. Precipitation of \( \alpha \) phase
V. Dissolution of \( \alpha \) phase
VI. Above \( \beta \)-transus temperature – \( \beta \) phase
ω observed by 3D atom probe

• Observation is based on chemical differences

Deveraj et al., Scripta Mat 61 (2009)
Hardening of Titanium

1. Inertstitial oxygen atoms
   – If oxygen content in pure Ti is increased from 0.18 to 0.4 wt. % →
   – → the strength is increased from 180 MPa to 480 MPa (!)
   – Typical oxygen content in commercial Ti alloys is 0.08 – 0.20 hm. %
   – Higher oxygen content often causes embrittlement
   – Positions of oxygen atoms are correlated to vacancies
     • positron annihilation spectroscopy study

2. Solid solution strengthening
   – $\alpha$-stabilizing substitutional elements (Al, Sn) strengthen $\alpha$–phase (Ti-5Al-2.5Sn $\rightarrow$ 800 MPa)
   – Some fully soluble $\beta$-stabilizing elements strengthen $\beta$–phase (Mo, Fe, Ta), others have negligible effect (Nb)
   – Size of the atoms and electron structure is decisive for this effect
     • Some atoms serve as obstacles for dislocation motion
Hardening of Titanium

3. Intermetallic particles (precipitation hardening)
   – Eg. Aluminides nitrides, carbides, silicide – and many others
   – Size of the particles and their distribution are crucial for the strengthening effect (Orowan strengthening)

4. Dislocation density and grain refinement
   – Forming/working (e.g. extrusion, forging, etc.) can increase dislocation density and cause grain refinement
   – Dislocations cause obstacles to movement of other dislocations causing increase strength
   – Grain and sub-grain boundaries may also act as dislocation obstacles
   – Working must be done at sufficiently low temperatures to suppress extensive grain growth and dislocation annihilation
Hardening of $\alpha+\beta$ alloys

- Sufficient content of Al (or Sn) leads to formation of $\text{Ti}_3\text{Al}$ particles (when content of Al is above 9 wt. %)
  - Solvus of $\text{Ti}_3\text{Al}$ particles is approx. 550°C, final annealing temperature must be below this temperature

- $\text{Ti}_3\text{Al}$ particles are hexagonal and coherent and block the dislocation movement causing precipitation hardening
  - In $\alpha+\beta$ alloys occurs separation of elements during annealing – $\alpha$-stabilizers diffuse to $\alpha$-phase, whereas $\beta$-stabilizers diffuse to $\beta$-phase
  - Intermetallic particles ($\text{Ti}_3\text{Al}$) can be created in $\alpha$-phase due to sufficient amount of $\alpha$-stabilizer despite overall (average) chemical composition does not allow such precipitation

- Phase boundaries serve as dislocation motion obstacles
  - The smaller are morphological features of respective phases, the bigger is strengthening effect
Hardening of metastable $\beta$–alloys

- Interstitial, solid solution and dislocation density strengthening
- Precipitation hardening/phase boundary hardening caused by phase transformation of $\beta$-matrix
  - Phase separation – $\beta_{\text{lean}} + \beta_{\text{rich}}$
  - Formation of $\omega$–phase particles
  - Precipitation of $\alpha$–phase particles
Lecture 2: Conclusion

- Titanium is polymorphous material – two stable phases
  - $\alpha$-phase– hexagonal close-packed (hcp)
  - $\beta$-phase– body-centered cubic (bcc)
- Below $\beta$-transus temperature - $\alpha$ phase is formed
- Pure Ti – at room temperature only $\alpha$-phase
- $\alpha + \beta$ alloys
  - At room temperature mix of phases $\alpha + \beta$
  - $\alpha$ phase formation cannot be suppressed
- Metastable $\beta$-alloys
  - After quenching - only $\beta$-phase
  - Upon annealing $\alpha$–phase is formed
- $\beta \rightarrow \alpha$ transformation
  - Martensitic followed by growth ($\alpha + \beta$ alloys)
  - Precipitation followed by growth ($\beta$ alloys)
- $\omega$ phase
  - Nano-sized particles, precursor for $\alpha$-phase particles precipitation
- Hardening of Ti and Ti alloys
  - Pure ti is hardenend mainly by oxygen content
  - Alloys are hardened by solid solution strengthening, intermetallic particles and particles of other phases
Titanium and titanium alloys

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Thank you!

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