Titanium and titanium alloys

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Lecture 1

Titanium: properties and applications

- Titanium as element
- History
- Titanium in nature
- Isolation of titanium from minerals
- Industrial production
- Principal properties
- Applications
Titanium as element
Titanium as element

- Light metal with typical metallic gray color
- Symbol: Ti
- Atomic number: 22
- Relative atomic weight 47.867
- Melting point: 1941 K, 1668°C
- Boiling point 3560 K, 3287°C
- Density: 4.5 kg/dm³ (Fe = 7.8 kg/dm³, Al = 2.7 kg/dm³)
- Electron configuration: [Ar] 3d² 4s²
  - Transition metal
  - Likely to have oxidation number IV (TiO₂ extremely stable)
Some history

• **1791** – Titanium discovered by English chemist William Gregor in mineral Ilmenite (FeTiO$_3$)

• **1795** – Impossible to isolate Ti from minerals → therefore called by Martin Klaproth in honor of Titans – gods of Ancient Greek mythology

• **1910 (!)** – finally isolated by heating titanium tetrachloride (TiCl$_4$)

• **WWII** – first applications – parts of military aircrafts

• **1950s** – still the most used alloy Ti-6Al-4V developed in Soviet Union, however very soon produced also in USA

• **1950s – 60s** onward of applications in military and civilian aircraft industry and in space programme

• **60s – now** development and production of new alloys in USA, Russia and Japan

• **90s – now** - massive production in China
Titanium in the nature and titanium white

TiO₂ – titanium white
- High brightness, reflectivity, high refractive index, absorbs UV radiation
- Used as white pigment – col-lours and coatings, plastics, paper, inks, cosmetics, pharmaceuticals, artificial food pigment E171
- Worldwide yearly production – 4 milions tonnes (vs. only 186 thousand tonnes of Ti)

Rutile - TiO₂
Anatase - TiO₂
Ilmenite - FeTiO₃
Isolation of Titanium

- Common metallurgical approaches are not usable in the case of Titanium

- Titanium is extremely reactive with oxygen, hydrogen, carbon and nitrogen under elevated temperatures

- Titanium is manufactured by reduction of TiCl₄ gas employing magnesium in the atmosphere of inert argon (Kroll’s process)

- FeTiO₃ + H₂SO₄ → Fe₂(SO₄)₃ + TiOSO₄

  TiOSO₄ → TiO₂ + SO₄

  TiO₂ + 2Cl₂ → TiCl₄ + O₂

  TiCl₄ + 2Mg → Ti + 2MgCl₂

  • Titanium is separated by high-temperature vacuum annealing from the mixture of titanium, magnesium dichloride and remaining magnesium

  • Magnesium dichloride is decomposed to Mg and Cl via electrolysis and both component can return into the process

  • Resulting material is brittle and porous substance (→ titanium sponge)

  • → Titanium is expensive
Industrial production

- Titanium sponge is subsequently crashed and milled
- Compact material (either pure metal or an alloy) can be produced by melting under high vacuum or very clean inert atmosphere (He, Ar)
- Typical size of one batch – 5-10 tonnes
- → Titanium is expensive
  - Ti: 25$/kg
  - Cu: 8$/kg
  - Al: 1$/kg
  - Ag: 30$/kg
  - Ta: 380$/kg
Titanium production in the world

- Titanium is the ninth most plentiful element of Earth crust (0,63 wt. %) – seventh within the metals
- Current estimated reserves of titanium would be sufficient for following 3000 years (considering current production)
- China currently is and is going to be in the future the biggest producer of titanium sponge in the world
  - Cheap labour and energy
  - No environmental concerns

**Production of rutile and ilmenite (2011)**

**Production of Ti (2011)**
Principal properties - overview

• Light gray metal
• Comparatively low density (when compared to steels)
• Comparatively high strength (similar to that of steels)
• **Low thermal conductivity** (➔ complicates machining)
• Extremely high corrosion resistance – very stable metal
• High reactivity with gases (➔ complicates thermal/thermomechanical treatment)
• Non-toxic element (➔ applicable in medicine)
Specific density/specific strength

- Strength of titanium and titanium alloys is similar to that of steels
- Titanium is, however, twice lighter
  - I.e. has lower specific density
  - I.e. has higher specific strength

<table>
<thead>
<tr>
<th></th>
<th>(\rho) [g/cm(^3)]</th>
<th>(\sigma) [MPa]</th>
<th>Spec. (\rho) [g/cm(^3)/kPa]</th>
<th>Spec. (\sigma) [MPa.cm(^3)/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>4.5</td>
<td>400 - 1400</td>
<td>11 - 3</td>
<td>90 - 310</td>
</tr>
<tr>
<td>Steels</td>
<td>8</td>
<td>400 - 1500</td>
<td>20 - 5</td>
<td>50 - 190</td>
</tr>
<tr>
<td>Al</td>
<td>2.7</td>
<td>100 - 300</td>
<td>27 - 9</td>
<td>40 - 110</td>
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Thermal and electric conductivity

- Titan is a bad electric conductor.
- Extremely low thermal conductivity seriously complicates machining, cutting, drilling, etc.

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<th>Thermal conductivity [W m⁻¹ K⁻¹]</th>
<th>Electric resistivity [μΩ m]</th>
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<tbody>
<tr>
<td>Ti</td>
<td>7 - 20</td>
<td>0.4 – 1.7</td>
</tr>
<tr>
<td>Fe</td>
<td>80</td>
<td>0.09</td>
</tr>
<tr>
<td>Al</td>
<td>237</td>
<td>0.03</td>
</tr>
</tbody>
</table>
Corrosion resistance

- Corrosion potential of titanium (-1.63 V) is similar to that of aluminum, titanium is therefore not considered a noble metal
- **Excellent corrosion resistance** is achieved by perfect passivation by surface layer of TiO$_2$
- Titanium is resistant in long-term to atmospheric conditions, sea water, body fluid or even more aggressive environments
- For the same reason, titanium is resistant to standard etchants – the most utilized etchant is a mixture of nitric and fluoric acids (HF + HNO$_3$)
  - HF – increases the etching rate and HNO3 decreases (stabilizes) the etching rate
  - be careful both acids are being consumed during the etching and etching rate may suddenly rise
- In biological environment (body fluid), titanium behaves as inert, non-toxic material
Main applications - overview

• **Aerospace industry** - jet engines, aircraft construction
  – Why? – High specific density

• **Pipes** – chemical and petrochemical industry,…
  – Why? – Unaltered corrosion resistance

• **Part of deep-sea oil wells**
  – Why? – Low specific density, excellent corrosion resistance

• **Medicine** – orthopaedic implants, fixing devices
  – Why? – Non-toxicity, high strength

• **Sporting goods** – golf clubs, tennis rackets, bicycles
  – Why?– High strength accompanied by relatively low elastic modulus

• **Jewellery, architecture, outdoor equipment**
Application in aerospace industry

• The first commercial application of titanium alloys – since the mid of 1950s
  – Aircraft industry and space program
• Ti content in aircraft construction
  – Airbus – 5% of mass is Ti
  – Boeing – 10% of mass is Ti
  – Carbon composite (Boeing 787 – Dreamliner) are used at the extent of aluminum
    – relative content of Ti is still growing
• Aircraft engines
  – 25% of mass is Ti (service temperature up to 500°C)
Titanium pipes

• High corrosion resistance of Ti
  – Resistance to aggressive environments → application in chemical and petrochemical industry
  – service-free pipes with prolonged life-time
• Main limitation is high price
• Commercially pure Ti is often used (cheaper than alloys)
• Manufactured mainly in China – mining, sponge production and manufacturing of final product at one place
Deep-sea oil wells

• Deep-sea oil wells – available only thanks to Ti
• Low specific density is the key advantage (note that effect of low density is even pronounced when immersed to the water)
• High corrosion resistance to sea water
• Drilling device itself cannot be made of Ti – low thermal conductivity
• Recent exploration of sub-ice lake in Antarctica – titanium drilling machine
Automobile industry

• Mass savings of 50% when compared to steel
  – But price

• Emerging field of possible applications
  – Huge emerging market for Ti
  – But price of final products must decrease

• Springs– low elastic modulus of Ti is utilized
  – Even bigger mass savings (up to 70%)
  – Better driving properties
  – e.g. Volkswagen Lupo
Application in medicine

• Total endoprostheses of big joints (hip, knee)
  – → high strength, non-toxicity and low elastic modulus
    (compared to steels of Co-Cr alloys)
• Fixation of complicated bone-fractures
• Fixation and supportive devices in the cases of degenerative illnesses (including bone cancer)
• Dental implants
Sporting goods

- **Golf** clubs – lower density of titanium allows manufacturing bigger golf club for better contact with the ball
- **Tennis** rackets (optimal combination of strength and stiffness)
- **Bicycles**
- Racing cars, racing motorcycles, racing (and non-racing) wheelchair
- **Scuba diving** oxygen tanks, softball bats
Architecture

- Stable gray metallic color or:
- Wide spectrum of colors can be achieved by anodization
  - Thanks to thin layer of oxides
- Long-term stability under atmospheric conditions

Guggenheim museum, Bilbao
Fukuoka Dome, Japan
Jewellery

- Watches and jewellery
  - Typical metallic gray color
  - Elimination of allergic skin reactions
  - High stability of cover – prolonged life-time
  - Strong and hard (compared to gold and silver)
Outdoor equipment

• Cookware and cutlery for camping/outdoor
  – Extremely low weight (compared to both steel and aluminum)
  – Absolutely non-toxic (vs. aluminum))
  – Disadvantage: extremely low thermal conductivity
Lecture 1: Conclusion

• There is plenty of titanium in minerals in the nature
• Isolation of titanium is complicated and expensive
• Titanium has unique properties
  – High strength, low density (4.5 g/cm³)
  – Excellent corrosion resistance
• Applications
  – Aerospace industry
  – Pipes and oil wells
  – Medicine, sporting goods, jewellery
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Thank you!
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Thank you!

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