THERMODYNAMICS OF MATERIALS AND PHASE EQUILIBRIA

COURSE PROJECT

Thermodynamics Aspects of Ti & Ti Alloys Nitriding

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OUTLINE

- Surface Engineering
- Diffusion Coatings
- Thermodynamic aspects of nitriding
  - Potential chemical reactions
  - Phase Diagrams analysis
    - Binary (Ti-N)
    - Ternary (Ti-N-Al & Ti-N-V)
- Diffusion kinetics of nitriding
**Surface Engineering**

- Sub-discipline of materials science dealing with the surface of solid matters

**Solutions:**
- Heat treatments
- Thermochemical treatments (Diffusion layers)
- Coating
DIFFUSION COATINGS

- Diffusing various elements on surface of sample to have better properties due to new formed compounds and phases
  - Nitriding, Carburizing, Oxidation, Boriding

Different substrates: Steels, Cermets, Ti & Ti alloys (TiAl6V4)

Ani Zhecheva, UK, 2005
**THERMODYNAMIC ASPECTS OF NITRIDING**

**Ti-N Binary system**
- hexagonal close-packed (HCP) solid solution ($\alpha$Ti), with a wide range of compositions;
- the terminal body-centered cubic (BCC) solid solution ($\beta$Ti), with a wide range of compositions;
- the tetragonal $\text{Ti}_2\text{N}$ phase ($\epsilon$);
- the face-centered cubic (FCC) TiN phase ($\delta$), with a wide range of compositions.

- One peritectoid equilibrium: 
  $\alpha$(Ti) + TiN + $\text{Ti}_2\text{N}$
- Two peritectic equilibria:
  L + $\alpha$(Ti) + $\beta$(Ti)
  L + TiN + $\alpha$(Ti)

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**Plasma & Gas nitriding temperature range**

![Thermodynamic Diagram](image)

Calculated with Thermo-Calc, Calphad website

Y.S. Han, RU, 2004
**Thermodynamic Aspects of Nitriding**

**Ti & N**

The most probable reactions:

- \( \text{Ti(s)} + \frac{1}{2} \text{N}_2 \rightarrow \text{TiN(s)} \)
- \( 4\text{Ti(s)} + \text{N}_2 \rightarrow 2\text{Ti}_2\text{N(s)} \)

![Graph showing thermodynamic aspects of nitriding](image)
✓ Al & V are alloying elements at Ti64

✓ Considering their reactions with $N_2$

$$2Al+N_2 \rightarrow 2AlN$$

$$2V+N_2 \rightarrow 2VN$$

$$13V+3N_2 \rightarrow V_{13}N_6$$

H.A. Wriedt, USA, 1986
THERMODYNAMIC ASPECTS OF NITRIDING

✓ Vanadium & Nitrogen

13V + 3N₂ → V₁₃N₆

2V + N₂ → 2VN

O.N. Carlson, 1989
THERMODYNAMIC ASPECTS OF NITRIDING

- Availability of reaction elements
- Possibility of the reactions (thermodynamics, ΔG)
- Speed of the reactions (Kinetics)
THERMODYNAMIC ASPECTS OF NITRIDING

✓ Effect of alloying elements on the Ti-N phase diagram

α-stabilizer: raising the $\alpha \rightarrow \beta$ transition temperature

β-stabilizer: lowering the $\alpha \rightarrow \beta$ transition temperature

Better understanding: ternary and quaternary phase diagrams

Ani Zhecheva, UK, 2005
**THERMODYNAMIC ASPECTS OF NITRIDING**

✓ Ternary phase diagrams Ti-Al-N

- Binary compounds: AlN (hexagonal), TiAl₃ (tetragonal), Ti₅Al₁₁ (tetragonal), TiAl₂ (tetragonal), Ti₁₋ₓAlₓ (tetragonal), Ti₃Al₅ (tetragonal), TiAl (γ) (tetragonal), and Ti₃Al (α₂) (hexagonal), N-deficient mononitride TiN₁₋ₓ (δ) (cubic), Ti₂N (C4-type tetragonal) and δ’(ThSi₂-type tetragonal)
- Ternary compounds: Ti₃AlN₀.₅₆ (τ₁) (CaTiO₃), Ti₂AlN₀.₈₂ (τ₂), Ti₄AlN₀.₂₉ (Cr₂AlC)

Al-N-Ti isothermal section at 900 °C
N. Durlu, USA, 1997

Al-N-Ti isothermal section at 1000 °C
V. Raghavan, India, 2006
✓ The computed stability diagram at 1000 °C the partial pressure of \( N_2 \) against the mole fraction \( X_{Ti}/(X_{Ti} + X_{Al}) \)

✓ At the left end (Al rich), nitrogen remains dissolved in liquid Al at low pressures. As the pressure increases, \( \text{AlN} \) becomes stable.

✓ At the right end (Ti rich), nitrogen remains dissolved in (Ti) initially. As the nitrogen pressure increases, \( \text{Ti}_2\text{N} \) and \( \text{TiN}_{1-x} \) progressively become stable. The formation of \( \tau_1 \) is very sluggish, and in real-time process applications, \( \tau_1 \) may not form at all.

R. SCHMID-FETZER, 1994
THERMODYNAMIC ASPECTS OF NITRIDING

✓ Ternary phase diagrams Ti-V-N

- Only a few studies of the phase constitution in the N-Ti-V system are available. The alloys were prepared under argon by arc melting the nitrified vanadium alloys.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Composition, at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Terminal solid solution phases</strong></td>
<td></td>
</tr>
<tr>
<td>(αTi)</td>
<td>0 to ~3V, 0 to 23N</td>
</tr>
<tr>
<td>(βTi)</td>
<td>0 to 100V, 0 to 6.2N</td>
</tr>
<tr>
<td>(V)(α)</td>
<td>0 to 100Ti, 0 to 17N</td>
</tr>
<tr>
<td><strong>Intermediate phases</strong></td>
<td></td>
</tr>
<tr>
<td>Ti$_2$N(b)</td>
<td>33N</td>
</tr>
<tr>
<td>δTiN$_{1-x}$, δ(Ti, V)N</td>
<td>30 to 55N, 0 to 100V</td>
</tr>
<tr>
<td>5VN$_{1-x}$(c)</td>
<td>~33 to 50N, 0 to 100V</td>
</tr>
<tr>
<td>δTi$_2$N</td>
<td>38N</td>
</tr>
<tr>
<td>βV$<em>2$N$</em>{1-y}$(b)</td>
<td>29 to 31N</td>
</tr>
<tr>
<td>δ VN$_{1-x}$(b)</td>
<td>~43 to 46N</td>
</tr>
</tbody>
</table>

Assessed isothermal N-Ti-V at 1200 °C

M. Enomoto, Japon, 1991
**Diffusion kinetics of nitriding**

✓ Effect of alloying elements on nitrogen diffusion

- Nitrogen contents increase, get to highest value and then steep decrease is observed along the matrix. CpTi shows gentle decrease, but Ti alloys shows sudden decrease. Wide $\alpha$ shell region formed around TiN/$\alpha$ Ti region plays a role of a diffusion barrier.
- The diffusion of nitrogen is retarded by composite effects of alloy elements, particularly due to some $\alpha$ stabilizing elements contained in alloys.

W. Darjian, CA, 2001
Nitrogen diffusion at Ti alloys (atmosphere pressure)

Although in general the kinetics of impregnation of titanium alloys with nitrogen are described by a parabolic rule, the rate of growth of the nitride case is linear, for a short distance.

\[ x'_{\text{TiN}}(\tau) = 2w_{\text{TiN}} \sqrt{D_{\text{TiN}}^N \cdot \tau} \]

\[ x'_{(\alpha-\text{Ti}, N)}(\tau) = 2w_{(\alpha-\text{Ti}, N)} \sqrt{D_{\alpha-\text{Ti}}^N \cdot \tau} \]

\[ D_{\text{TiN}}^N = 0.8 \times 10^{-11} \frac{e^{-\frac{243000}{RT}}}{(\text{cm}^2/\text{sec})} \]

\[ D_{\alpha-\text{Ti}}^N = 0.2 \times 10^{-11} \frac{e^{-\frac{205300}{RT}}}{(\text{cm}^2/\text{sec})} \]

Comparison of \( D^N \) & growth rate of layers calculated by mentioned model and experimental data.
CONCLUSION

1. By using thermodynamic parameters and equilibrium phase diagrams for a system (like TiAl$_6$V$_4$ nitriding), investigation of the equilibrium phases at different temperatures and different chemical compositions is possible.

2. According to binary and ternary phase diagrams of Ti, Al, V and N, it seems there isn’t a lot of differences between equilibrium phases of pure Ti nitrided and Ti64 nitrided.

3. According to diffusion kinetics of nitrogen, the thickness of layers formed as a result of nitriding are different for pure Ti and Ti64.

4. Predicting the thickness of diffused layers is possible by using complicated modeling of nitrogen diffusion.

THANK YOU