Concordia University
Engineering and Computer Science

Thermodynamics of Materials and Phase Equilibria

Course Project

Thermodynamics Aspects of Ti & Ti Alloys Nitriding

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Presented by
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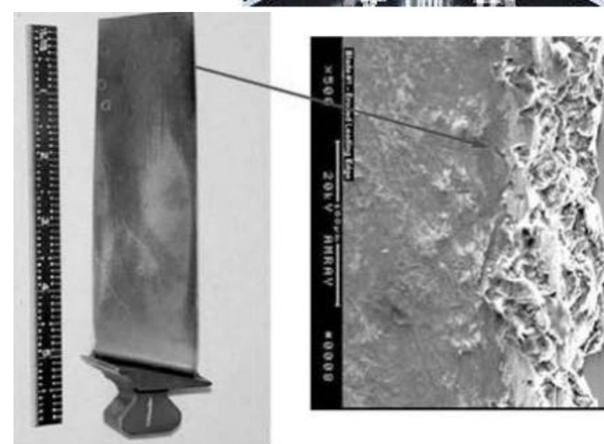
Outline

- 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

- Surface Engineering
  - Chemistry
  - Mechanical Engineering
    - Wear & Tribology
    - Erosion
      - Solid Erosion
      - Liquid Erosion
    - Corrosion
    - High temperatures
  - Electrical Engineering



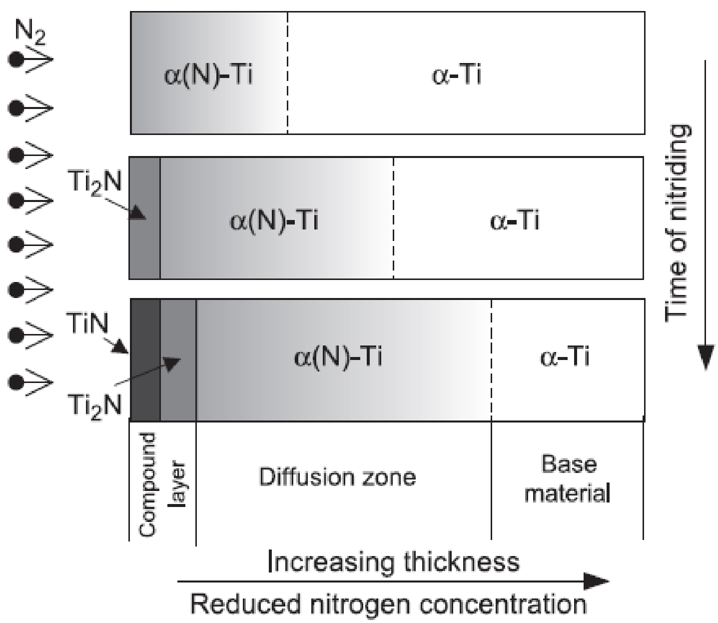
Solutions:

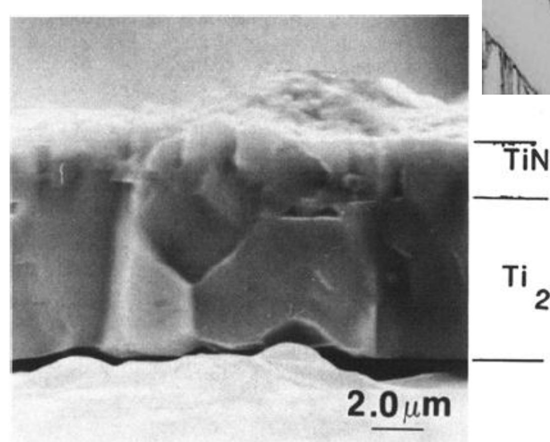
- **Heat treatments**
- **Thermochemical treatments (Diffusion layers)**
- **Coating**

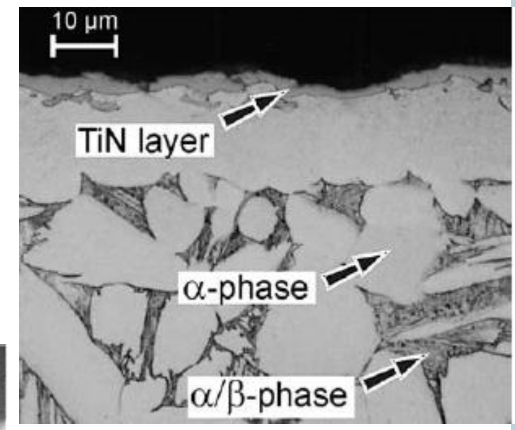
Diffusion Coatings

- **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)







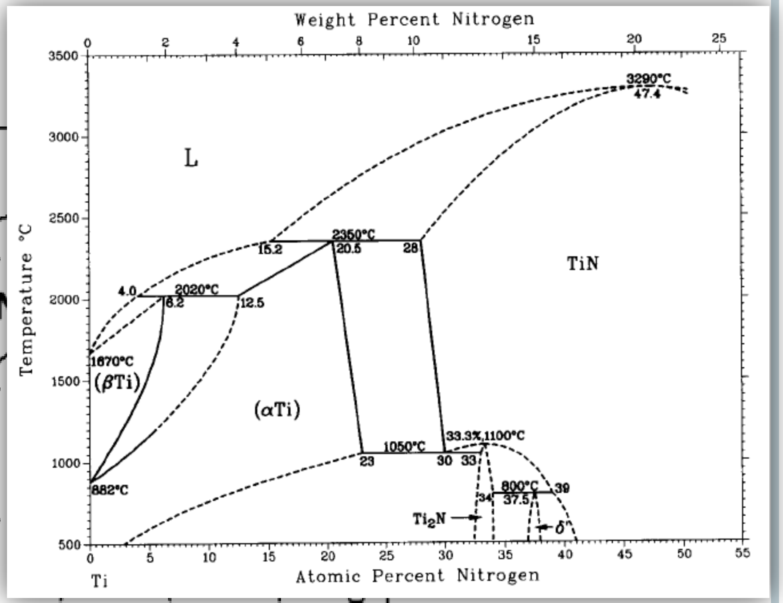
Ani Zhecheva, UK, 2005

THERMODYNAMIC ASPECTS OF NITRIDING

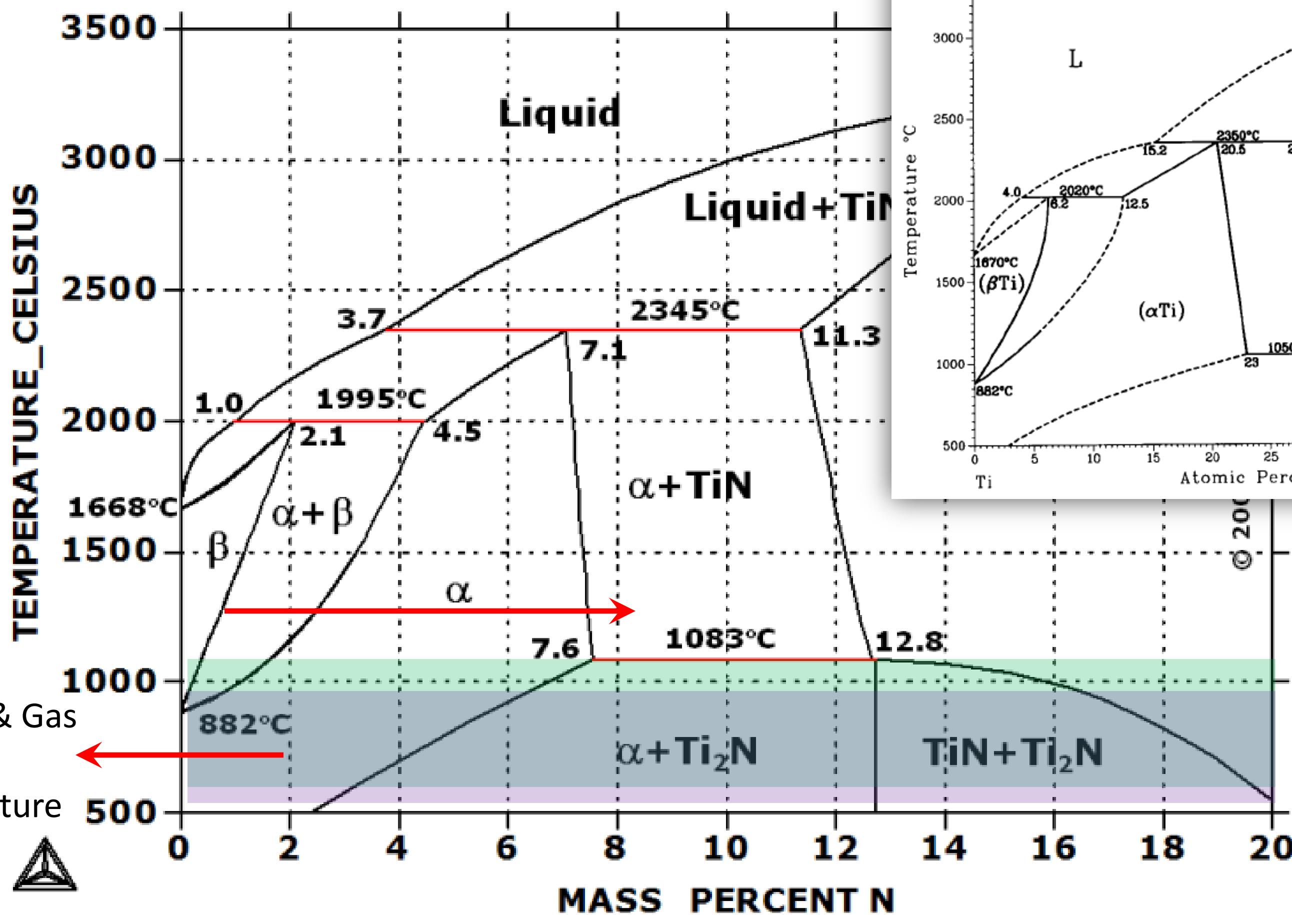
Ti-N Binary system

- **hexagonal close-packed** (HCP) solid solution (αTi), with a wide range of compositions;
- the terminal **body-centered cubic** (BCC) solid solution (βTi), with a wide range of compositions;
- the **tetragonal** Ti_2N phase (ε);
- the **face-centered cubic** (FCC) TiN phase (δ), with a wide range of compositions.

✓One peritectoid equilibrium:
α(Ti) + TiN + Ti_2N
✓Two peritectic equilibria:
L+ α(Ti)+β(Ti)
L+TiN+α(Ti)



Y.S. Han, RU, 2004



Plasma & Gas nitriding temperature range

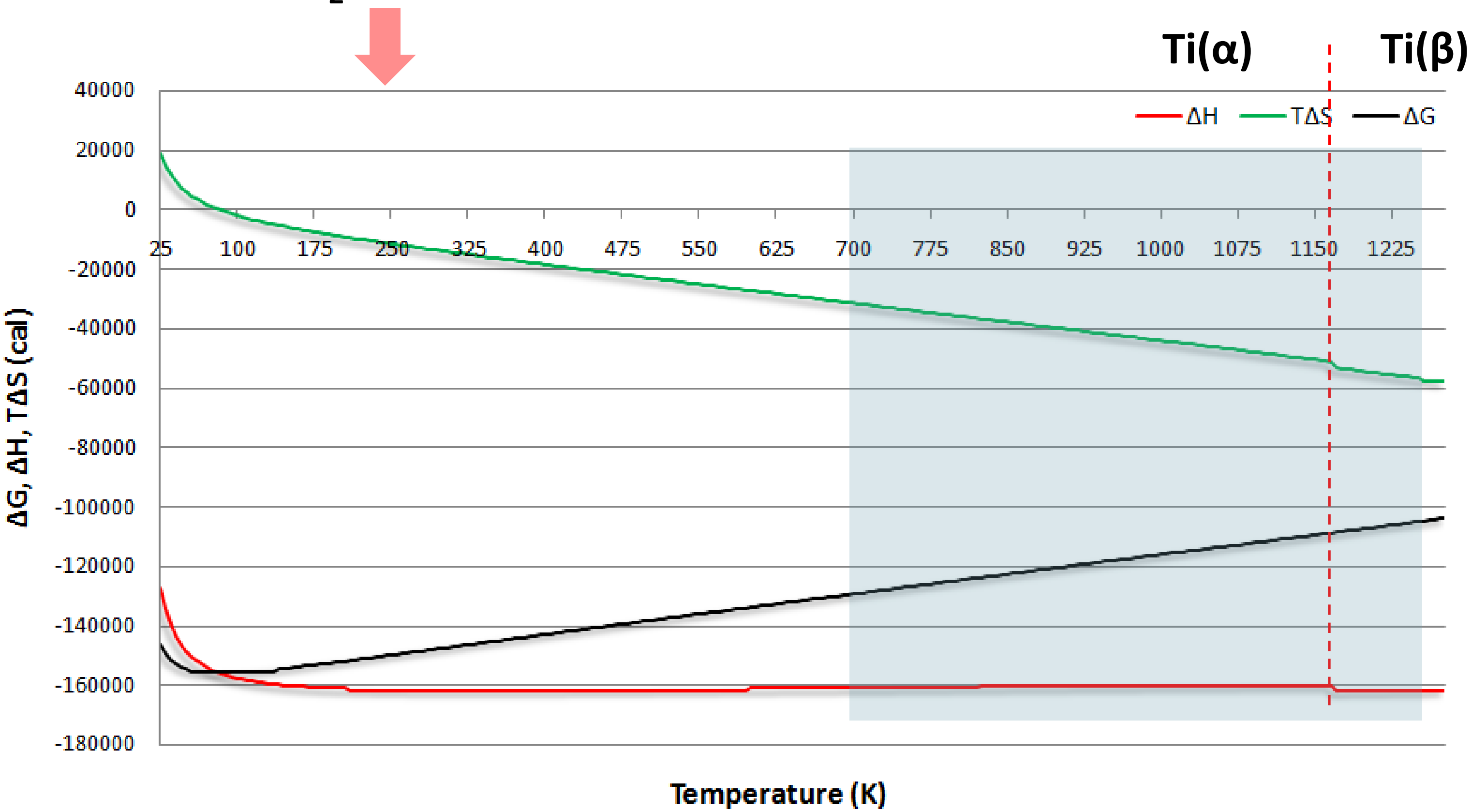
Calculated with Thermo-Calc, Calphad website

THERMODYNAMIC ASPECTS OF NITRIDING

Ti & N

The most probable reactions:

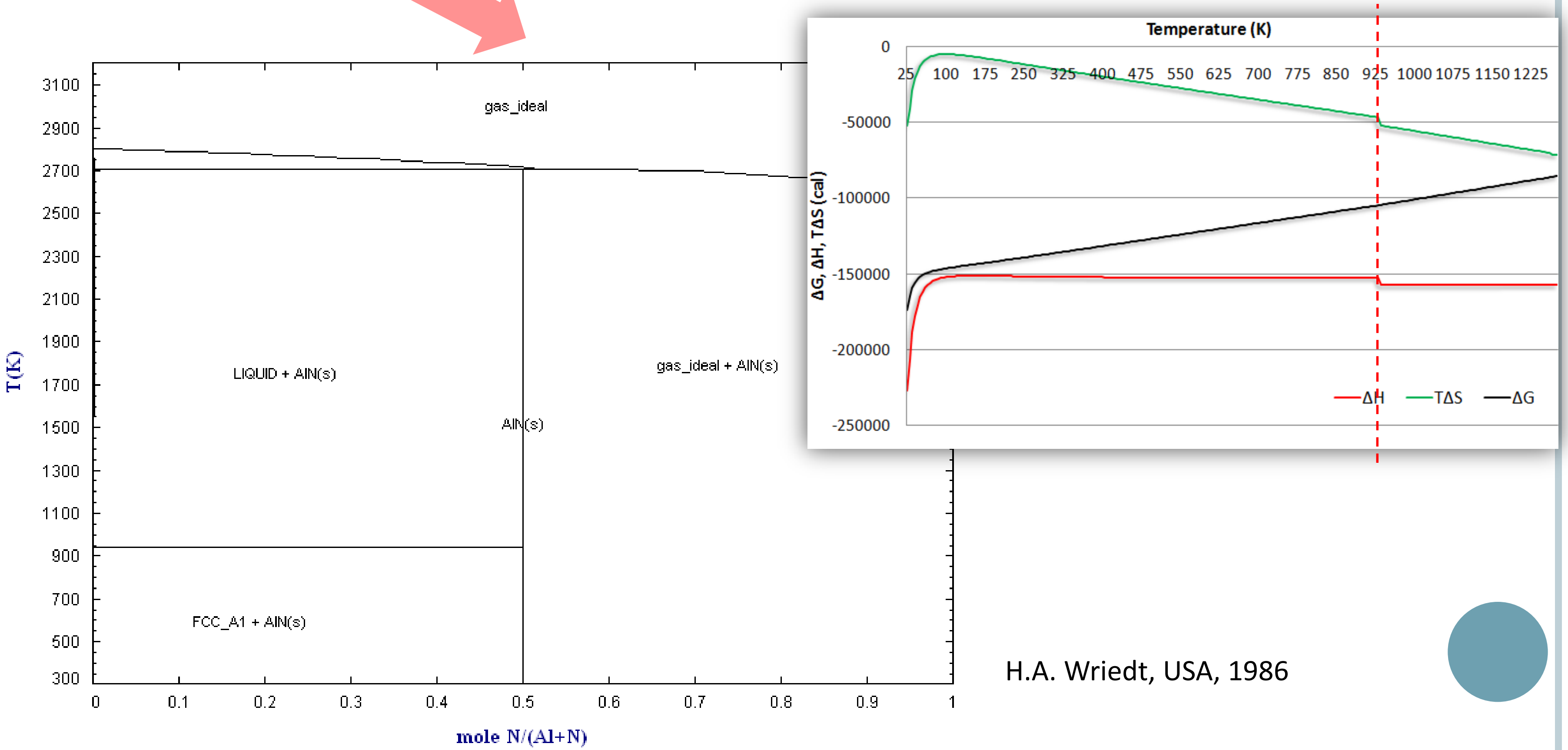
$$Ti(s) + 1/2\ N_2 \longrightarrow TiN(s) \qquad 4Ti(s) + N_2 \longrightarrow 2Ti_2N(s)$$



Thermodynamic aspects of nitriding

- ✓ **Al & V are alloying elements at Ti64**
- ✓ **Considering their reactions with N_2**

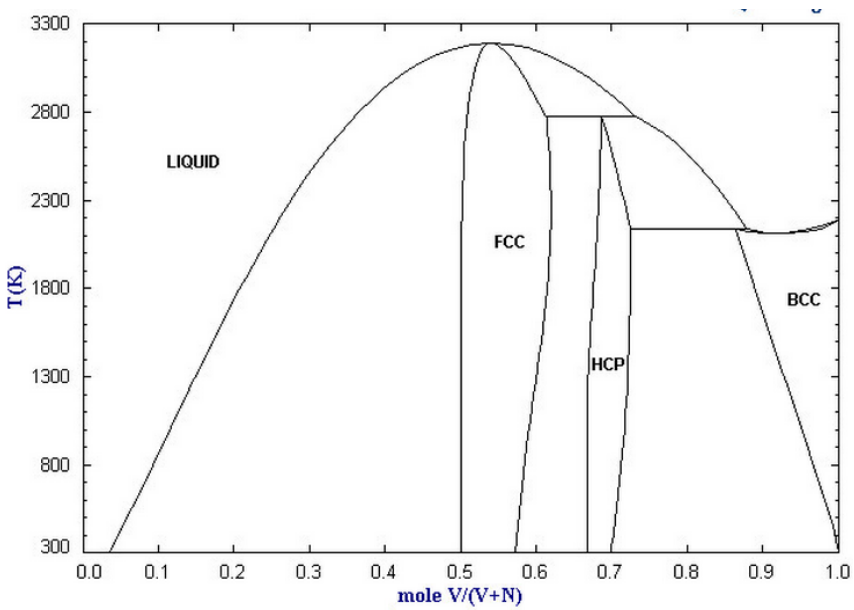
$2Al+N_2 \rightarrow 2AlN$ $2V+N_2 \rightarrow 2VN$ $13V+3N_2 \rightarrow V_{13}N_6$



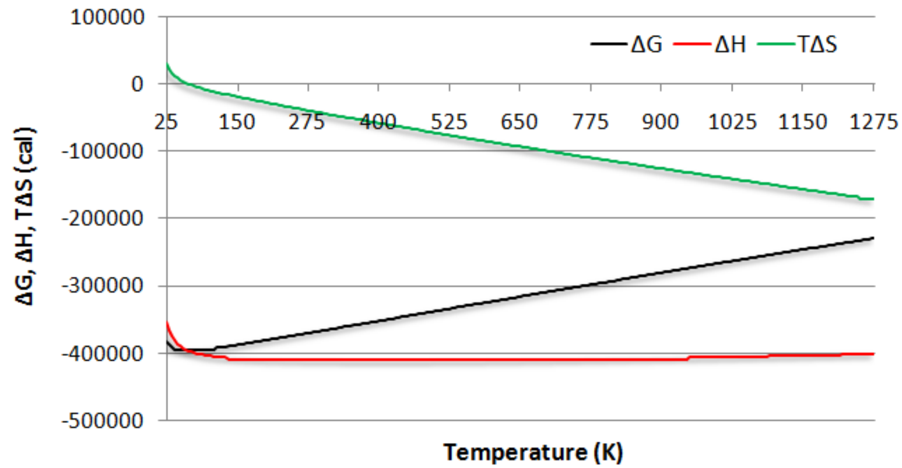
H.A. Wriedt, USA, 1986

THERMODYNAMIC ASPECTS OF NITRIDING

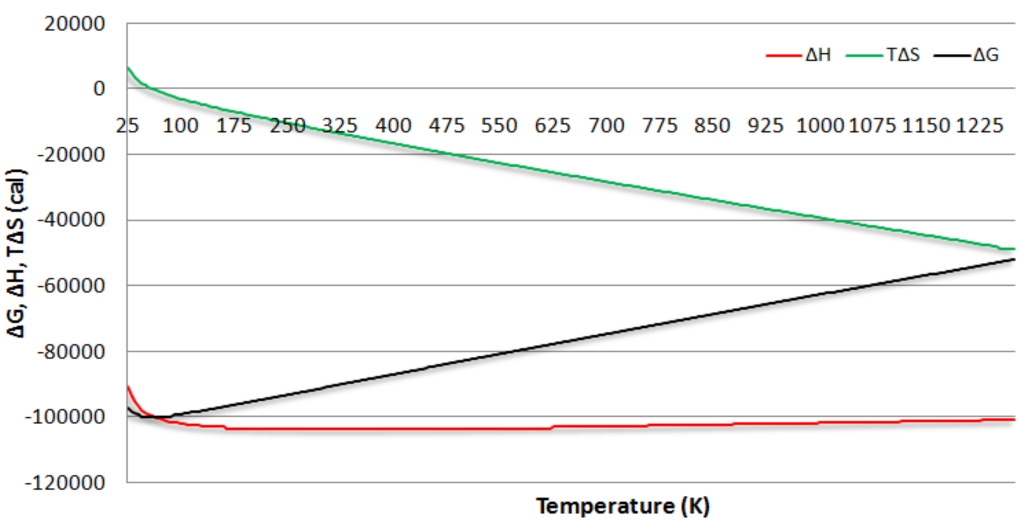
- ✓**Vanadium & Nitrogen**



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



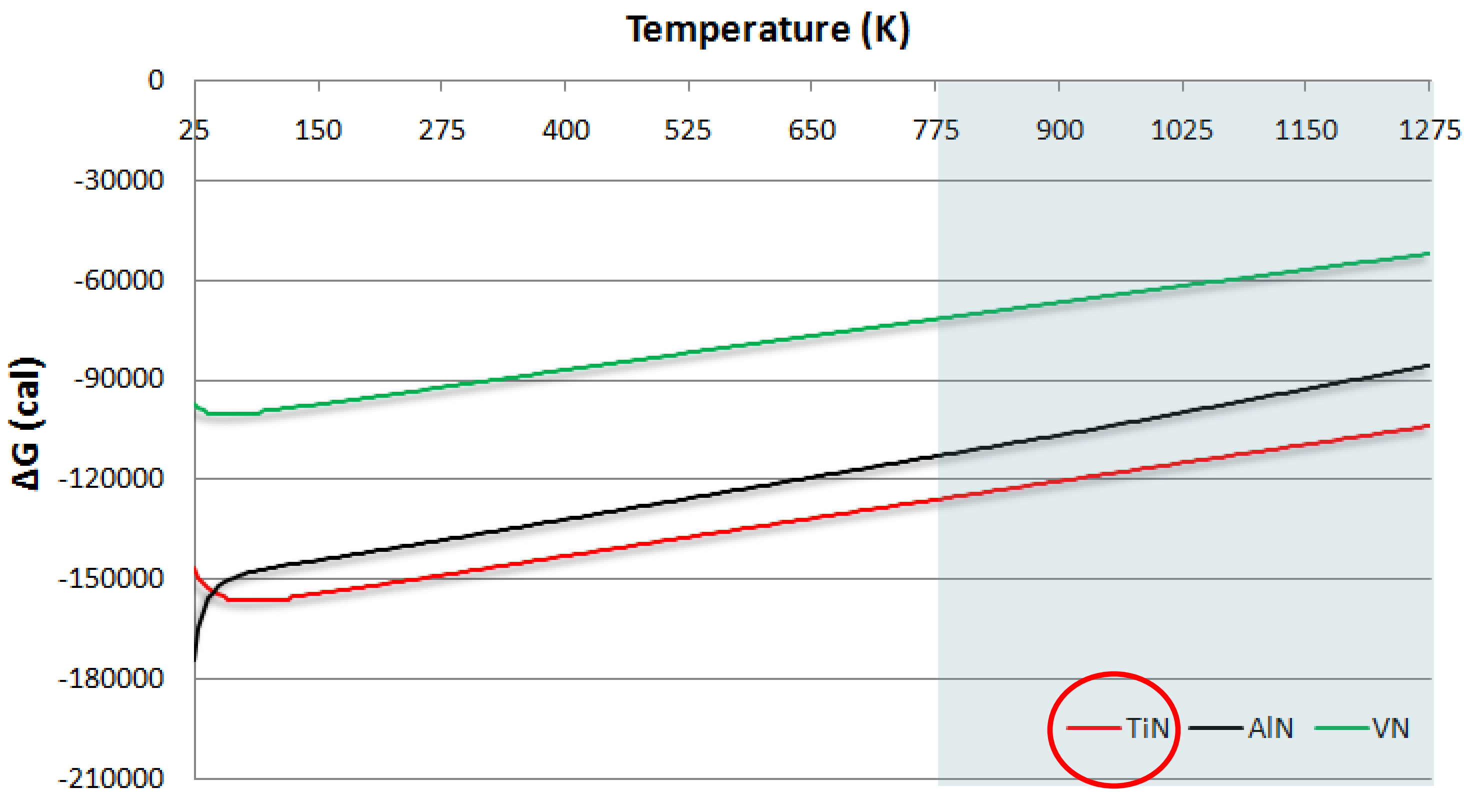
O.N. Carlson, 1989



$2V + N_2 \longrightarrow 2VN$

THERMODYNAMIC ASPECTS OF NITRIDING

- ✓ **Availability of reaction elements**
- ✓ **Possibility of the reactions (thermodynamics, ΔG)**
- ✓ **Speed of the reactions (Kinetics)**

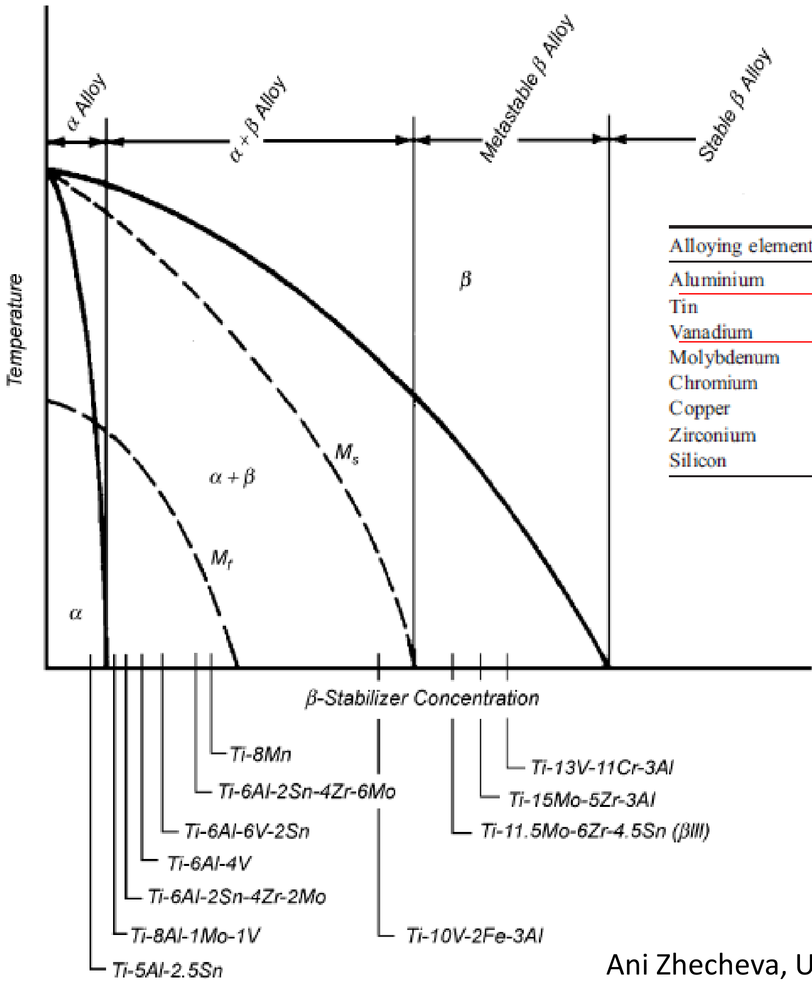


Thermodynamic aspects of nitriding

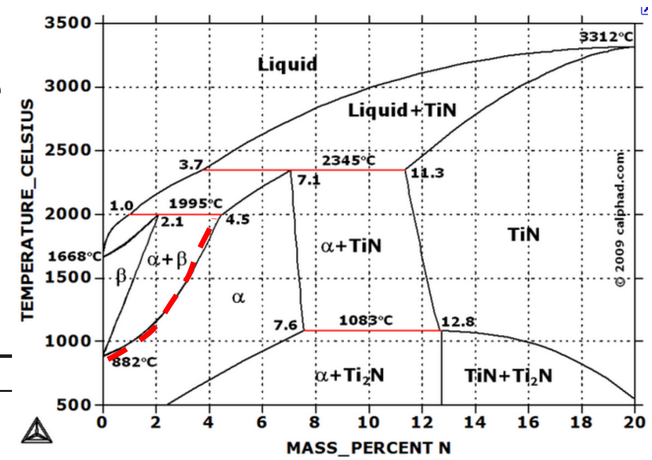
✓Effect of alloying elements on the Ti-N phase diagram

α-stabilizer: raising the α → β transition temperature

β-stabilizer: lowering the α → β transition temperature



Alloying element	Range (wt.%)	Effect on structure
Aluminium	2 to 7	α-stabilizer
Tin	2 to 6	α-stabilizer
Vanadium	2 to 20	β-stabilizer
Molybdenum	2 to 20	β-stabilizer
Chromium	2 to 12	β-stabilizer
Copper	2 to 6	β-stabilizer
Zirconium	2 to 8	α and β strengthening
Silicon	0.2 to 1	Improves creep resistance



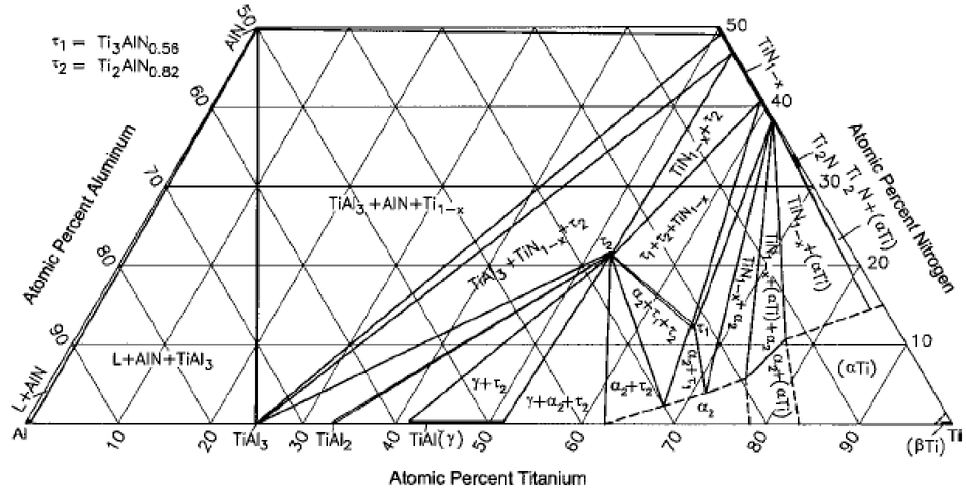
Better understanding:
ternary and quaternary phase diagrams

Ani Zhecheva, UK, 2005

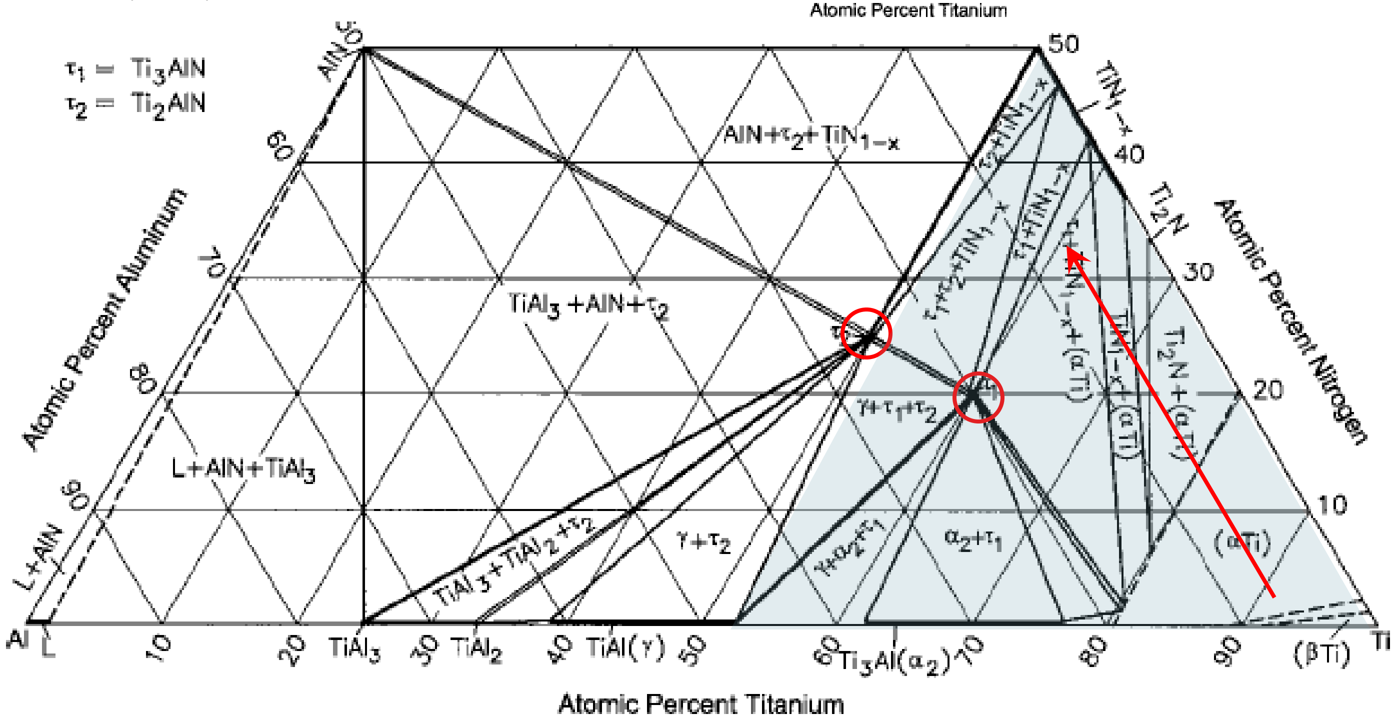
THERMODYNAMIC ASPECTS OF NITRIDING

✓Ternary phase diagrams Ti-Al-N

- Binary compounds: AlN (hexagonal), $TiAl_3$ (tetragonal), Ti_5Al_{11} (tetragonal), $TiAl_2$ (tetragonal), $Ti_{1-x}Al_{1+x}$ (tetragonal), Ti_3Al_5 (tetragonal), TiAl (γ) (tetragonal), and Ti_3Al (α_2) (hexagonal), N-deficient mononitride TiN_{1-x} (δ) (cubic), Ti_2N (C4-type tetragonal) and δ′($ThSi_2$-type tetragonal)
- Ternary compounds: $Ti_3AlN_{0.56}$ (τ_1) ($CaTiO_3$), $Ti_2AlN_{0.82}$ (τ_2), $Ti_4AlN_{0.29}$ (Cr_2AlC)



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



Al-N-Ti isothermal section at 1000 °C
V. Raghavan, India, 2006

THERMODYNAMIC ASPECTS OF NITRIDING

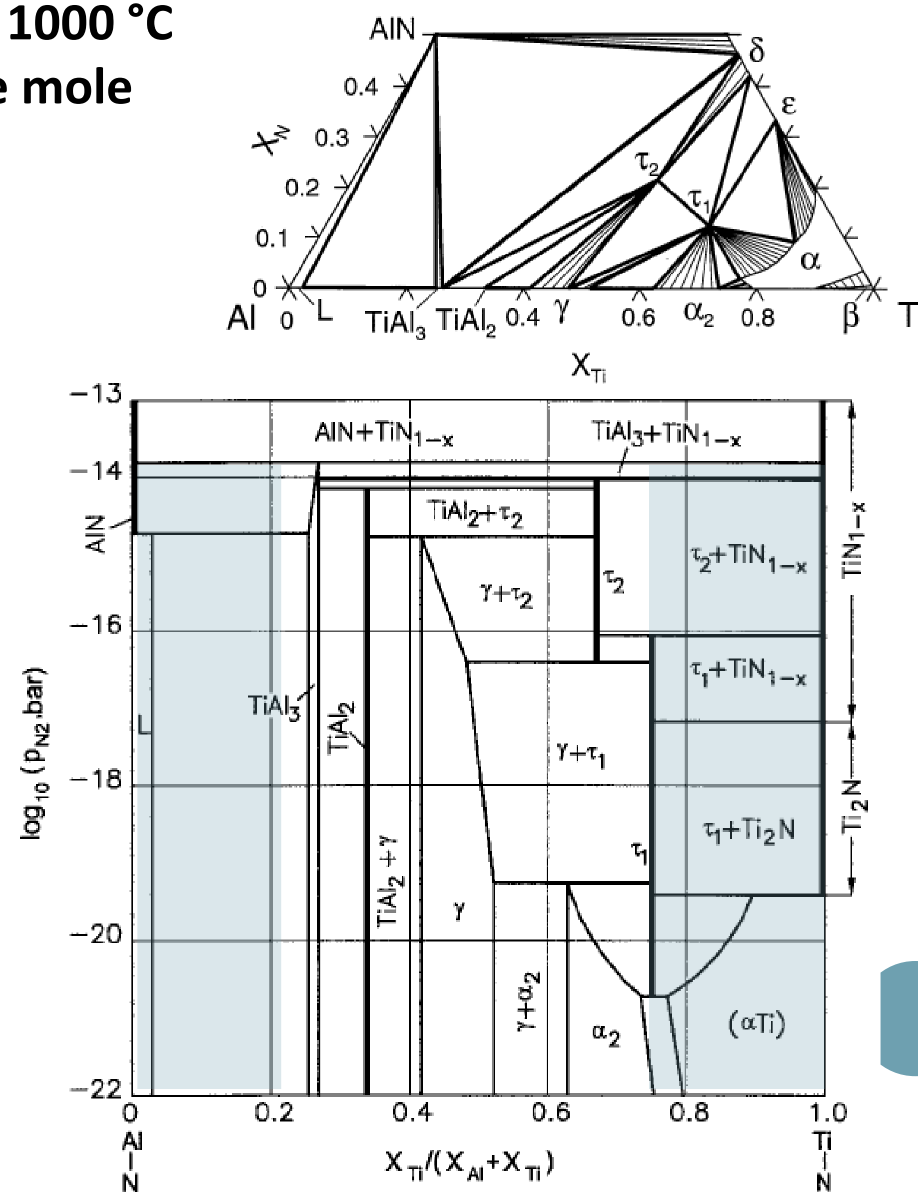
✓**The computed stability diagram at 1000 °C the partial pressure of N_2 against the mole fraction $X_{Ti}/(X_{Ti} + X_{Al})$**

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

✓At the right end (Ti rich), nitrogen remains dissolved in (Ti) initially. As the nitrogen pressure increases, **Ti_2N** and **TiN_{1-x}** progressively become stable.

The formation of **τ_1** is very **sluggish**, and in real-time process applications, **τ_1 may not form at all**.

R. SCHMID-FETZER, 1994



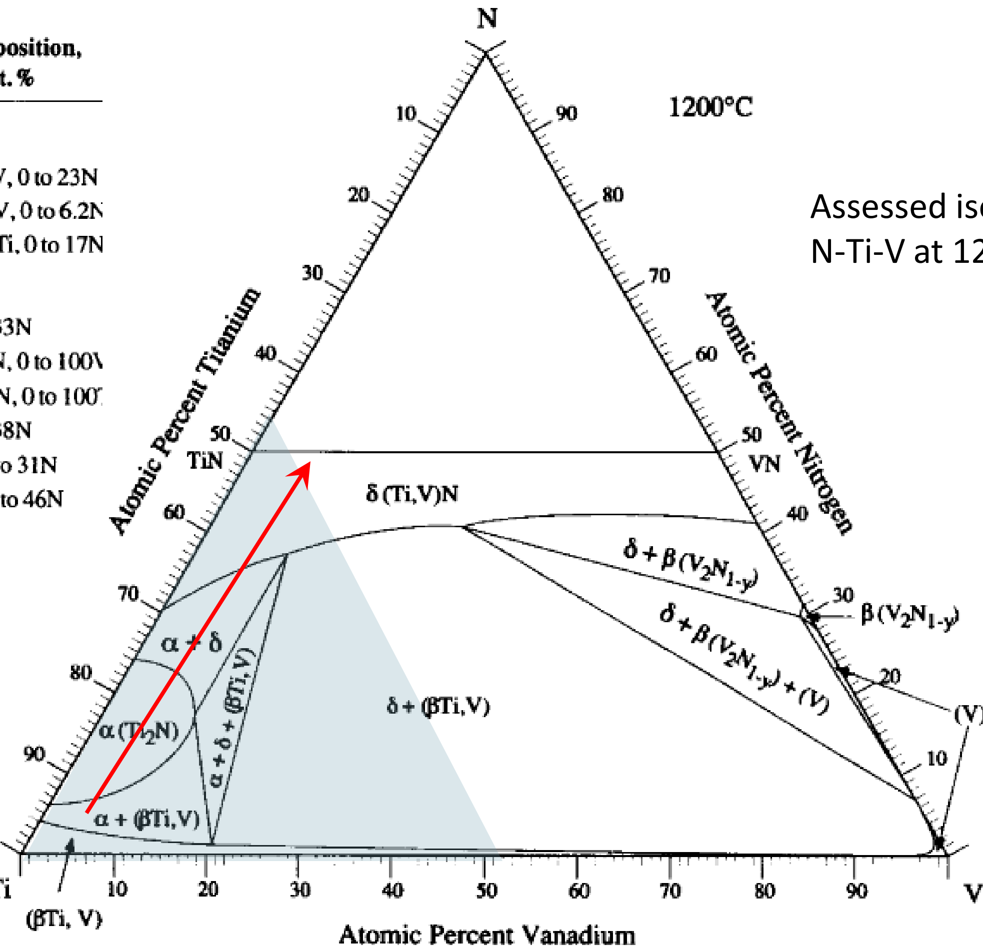
THERMODYNAMIC ASPECTS OF NITRIDING

✓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.

Phase	Composition, at. %
Terminal solid solution phases	
(αTi)	0 to ~3V, 0 to 23N
(βTi)	0 to 100V, 0 to 6.2N
(V)(a)	0 to 100Ti, 0 to 17N
Intermediate phases	
Ti_2N(b)	33N
δTiN_{1-x}, δ(Ti, V)N	30 to 55N, 0 to 100V
δVN_{1-x}(c)	~33 to 50N, 0 to 100
$\delta' Ti_2N$	38N
βV_2N_{1-y}(b)	29 to 31N
$\delta' VN_{1-x}$(b)	~43 to 46N

M. Enomoto, Japon, 1991

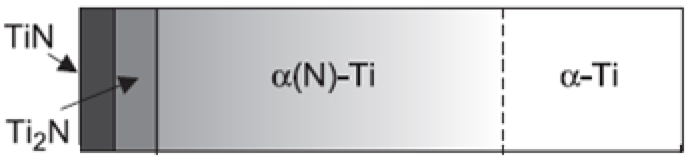


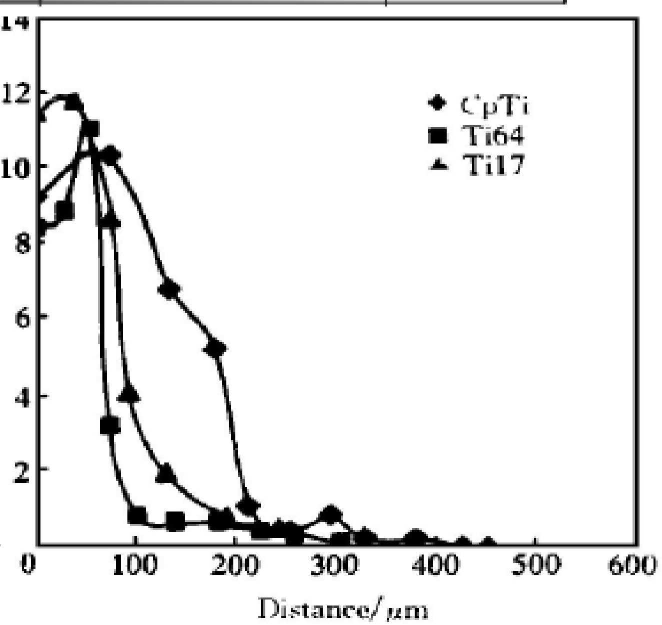
Assessed isothermal N-Ti-V at 1200 °C

DIFFUSION KINETICS OF NITRIDING

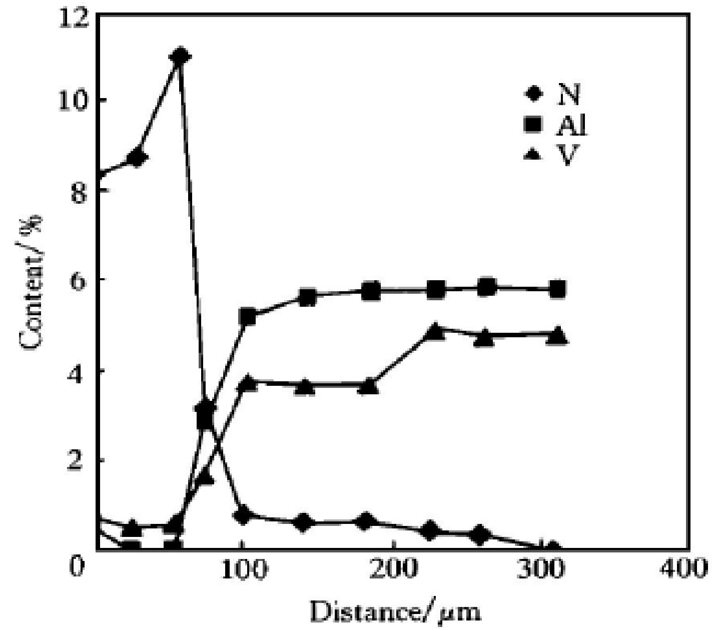
✓Effect of alloying elements on nitrogen diffusion

- 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 α shell region formed around TiN/α 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 α stabilizing elements contained in alloys.





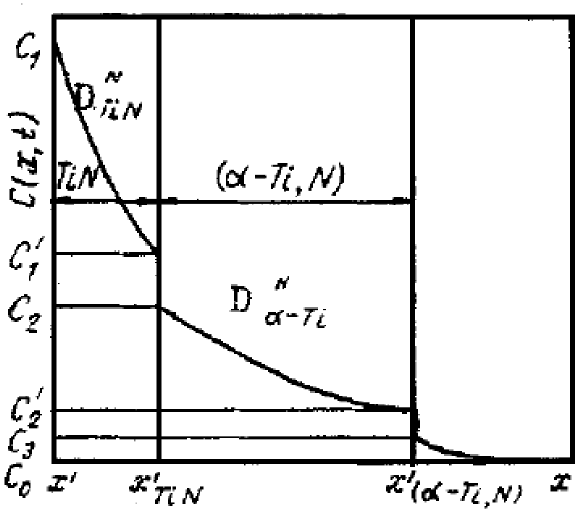
W. Darjian, CA, 2001



Diffusion kinetics of nitriding

✓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.**



$$x'_{TiN}(\tau) = 2\, w_{TiN} \sqrt{D^N_{TiN} \cdot \tau}$$

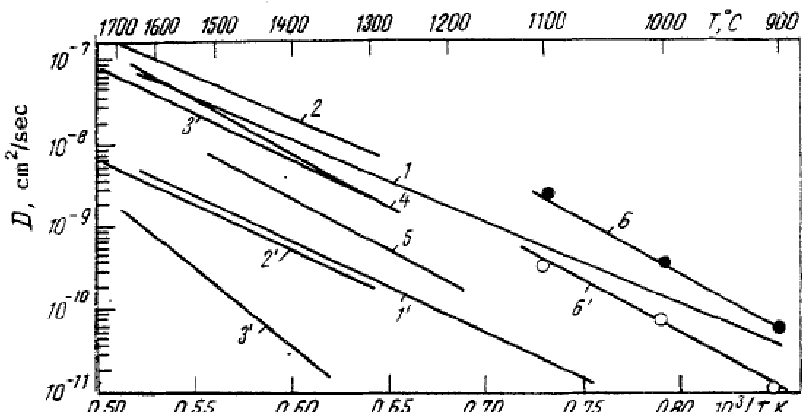
$$x'_{(\alpha\text{-Ti, N})}(\tau) = 2 w_{(\alpha\text{-Ti, N})} \sqrt{D^N_{\alpha\text{-Ti}} \cdot \tau}$$

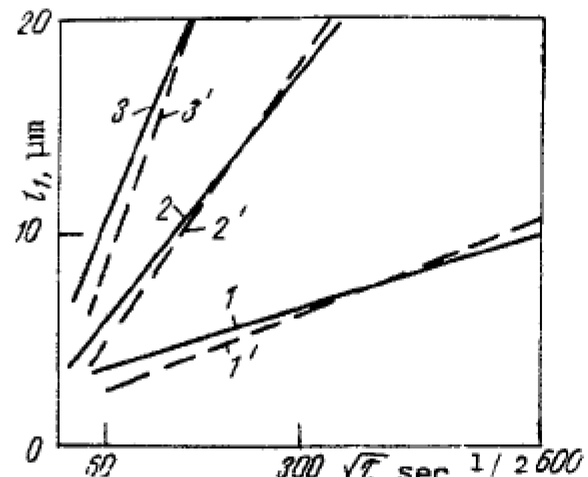
$$D^N_{TiN} = 0.8\, e^{-\frac{243000}{RT}} \ (\mathrm{cm^2/sec})$$

$$D^N_{\alpha\text{-Ti}} = 0.2\, e^{-\frac{205300}{RT}} \ (\mathrm{cm^2/sec})$$

G. G. Maksimovich, Ukraine, 1980

✓Comparison of D^N & growth rate of layers calculated by mentioned model and experimental





Conclusion

1. By using thermodynamic parameters and equilibrium phase diagrams for a system (like $TiAl_6V_4$ 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