Substitutional and Interstitial Diffusion in α_2-$Ti_3Al(O)$

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The reaction between Al_2O_3 and α_2-Ti_3Al was studied with a series of Al_2O_3/α_2-Ti_3Al multiphase diffusion couples annealed at 900, 1000 and 1100°C. The diffusion-paths were found to strongly depend on α_2-$Ti_3Al(O)$ composition. For alloys with low oxygen concentrations the reaction involved the reduction of Al_2O_3, the formation of a γ-TiAl reaction-layer and diffusion of Al and O into the α_2-Ti_3Al substrate. Measured concentration profiles across the interaction-zone showed “up-hill” diffusion of O in α_2-$Ti_3Al(O)$ indicating a significant thermodynamic interaction between O and Al, Ti or both. Diffusion coefficients for the interstitial O in α_2-$Ti_3Al(O)$ were determined independently from the interdiffusion of Ti and Al on the substitutional lattice. Diffusion coefficients are reported for α_2-$Ti_3Al(O)$ as well a γ-TiAl. Interpretation of the results were aided with the subsequent measurement of the activities of Al, Ti and O in α_2-$Ti_3Al(O)$ by Knudsen effusion-cell mass spectrometry.

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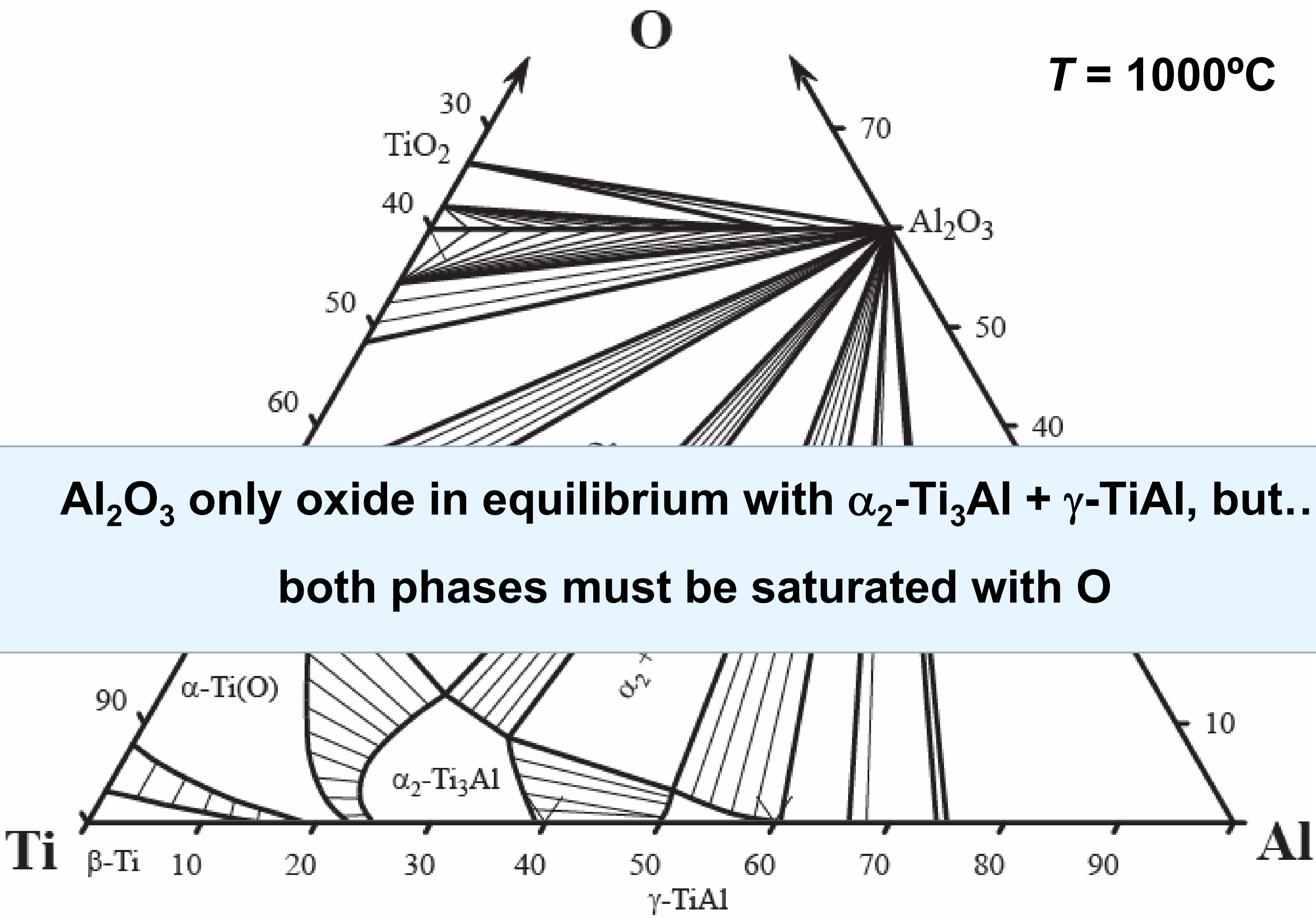
Ti-Al-O system



T = 1000ºC

Al_2O_3 only oxide in equilibrium with α_2-Ti_3Al + γ-TiAl, but…

both phases must be saturated with O

B. Lee, N. Saunders, *Z. Metallkd.*, 1997, **88**(2), pp. 152-161.

outline

- rationale… possible MMC and oxidation of α_2-Ti_3Al + γ-TiAl
- multi-phase couples: α_2 / Al_2O_3
    - ↪ results & calculations
- single-phase couples: α_2(O) / α_2(O)
    - ↪ results & calculations
- partial thermodynamic properties in α_2-Ti_3Al(O)
- summary

multi-phase Ti-Al / Al_2O_3 couples

- arc-melted: Al, Ti & TiO_2; annealed at T = 900, 1000, 1100ºC
  - ↳ closed system: Ta-foil (barrier for SiO)- in SiO_2 capsule
- HIP bonding (170 MPa, 1100ºC for 2 h), poly-crystalline Al_2O_3
  - ↳ re-encapsulated, reacted 900, 1000, 1100ºC for t = 20 ~ 500 h
- analysis: metallography, optical, EPMA and micro-hardness

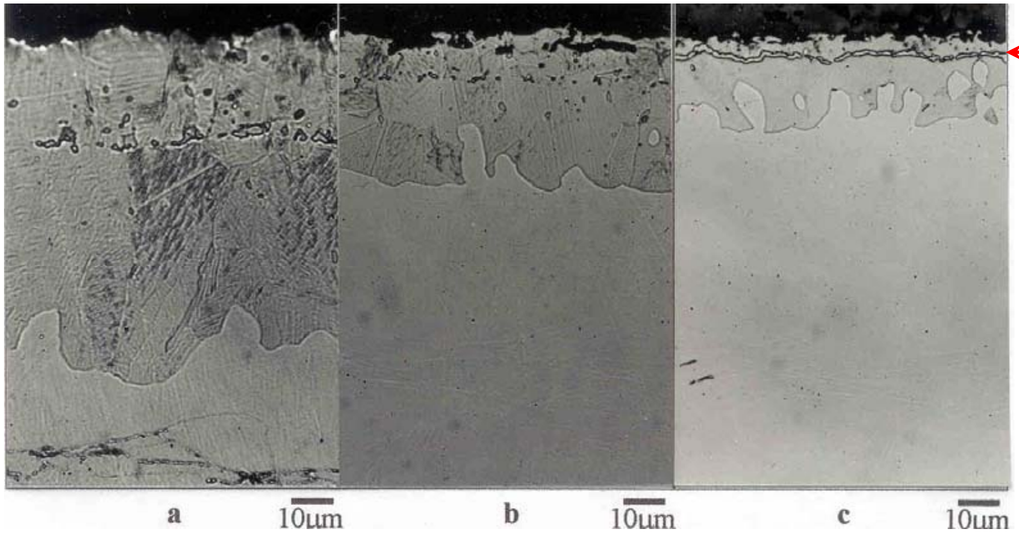
alloy	comp. (at.%)	phase	
1 ~ 3	Ti-(49, 52, 55)Al	γ-TiAl	← no reaction, ignore
4	Ti-25Al	α_2-Ti_3Al	
5	Ti-32Al	α_2-Ti_3Al	
6	TI-35Al	α_2-Ti_3Al	
7	Ti-33.35Al-5O	α_2-$Ti_3Al(O)$	
8	Ti-27Al-10O	α_2-$Ti_3Al(O)$	← reaction, but ignore
9 ~ 10	Ti-(40, 48)Al	$\alpha_2 + \gamma$	

α_2-Ti_3Al / Al_2O_3 couples

Al_2O_3

γ-TiAl

α_2-Ti_3Al

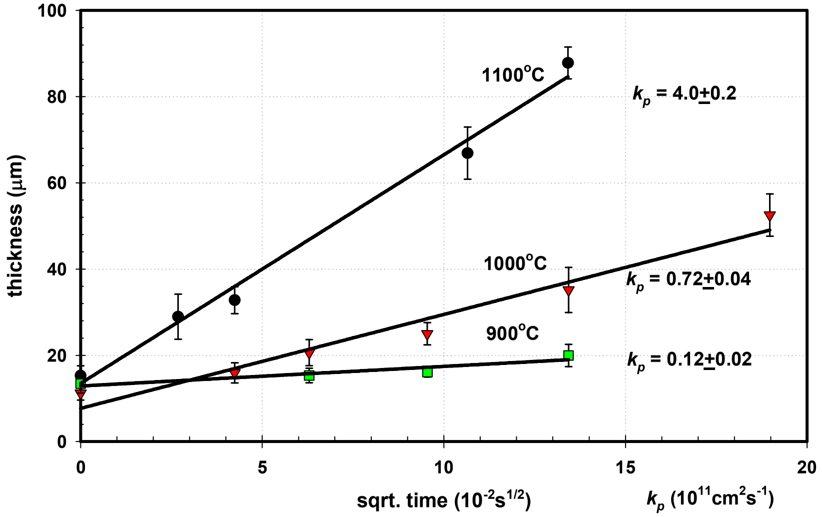


marker

Ti-32Al / Al_2O_3,

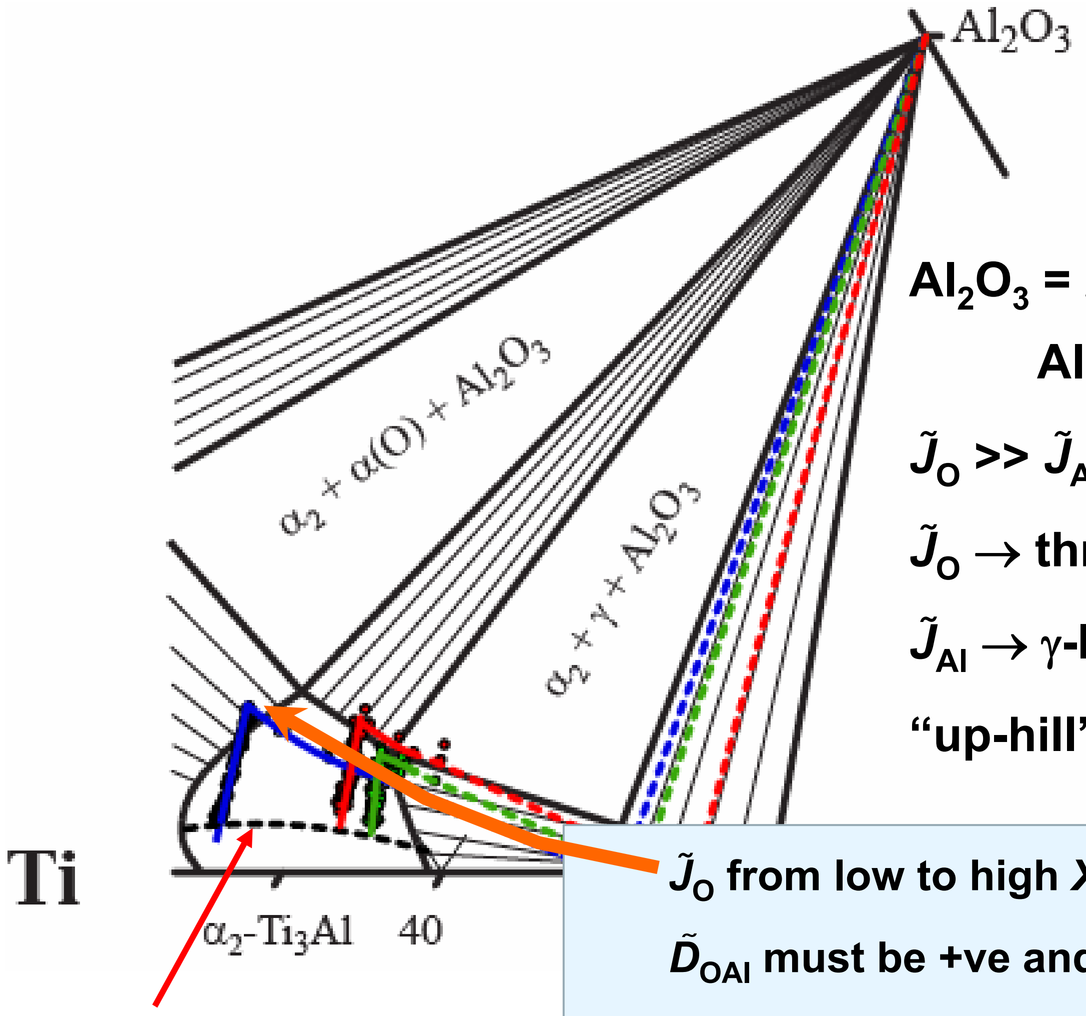
t = 500 h

1100ºC 1000ºC 900ºC



α_2-Ti_3Al / Al_2O_3 couples

T = 1100°C



EPMA error, TiO_2-layer

$Al_2O_3 = 2\underline{Al}_{\gamma,\alpha_2} + 3\underline{O}_{\gamma,\alpha_2}$ … "gas / solid"

Al, O supplied at activity of γ / Al_2O_3

$\tilde{J}_O >> \tilde{J}_{Al}$ (from diffusion path)

$\tilde{J}_O \rightarrow$ through γ-layer into $\alpha_2(O)$

$\tilde{J}_{Al} \rightarrow \gamma$-layer growth and enriches $\alpha_2(O)$

"up-hill" diffusion of O in $\alpha_2(O)$

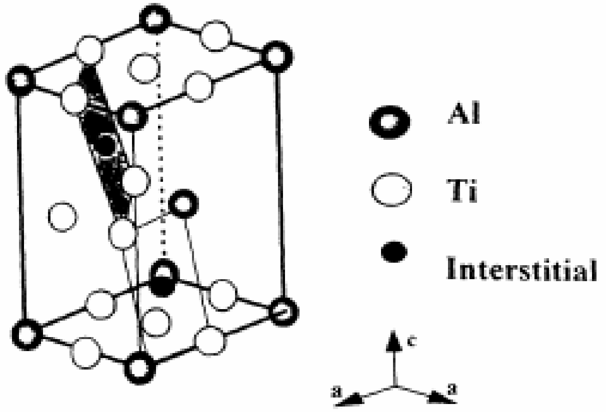
$\tilde{J}_O$ from low to high X_O: $\tilde{J}_O = -\tilde{D}^{Ti}_{OO}\frac{\partial C_O}{\partial x} - \tilde{D}^{Ti}_{OAl}\frac{\partial C_{Al}}{\partial x}$

$\tilde{D}_{OAl}$ must be +ve and significant…

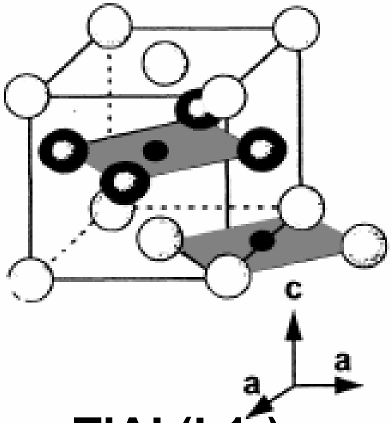
+ve thermodynamic interaction between O and Ti + Al

treating diffusion in Ti-Al-O

- Ti and Al substitutional; O interstitial, but [OTi$_6$] only stable sites
- limited kinetic interaction between lattices plus $\tilde{J}_O >> \tilde{J}_{Al}$, treat:
  - ↪ Ti-Al “pseudo binary” and O “transient equilibrium”



α_2-Ti$_3$Al (DO$_{19}$)



γ-TiAl (L1$_0$)

- correct profiles: r(Ti, Al) = 1.45, 1.43Å; $V_m(\alpha_2, \gamma) \approx 10.0$ cm^{3}mol^{-1}
  - ↪ Ti, Al: $C_i = \left(N_i / \left(N_{Ti} + N_{Al}\right)\right)/V_m$
  - ↪ O: $C_O = N_O / V_m$

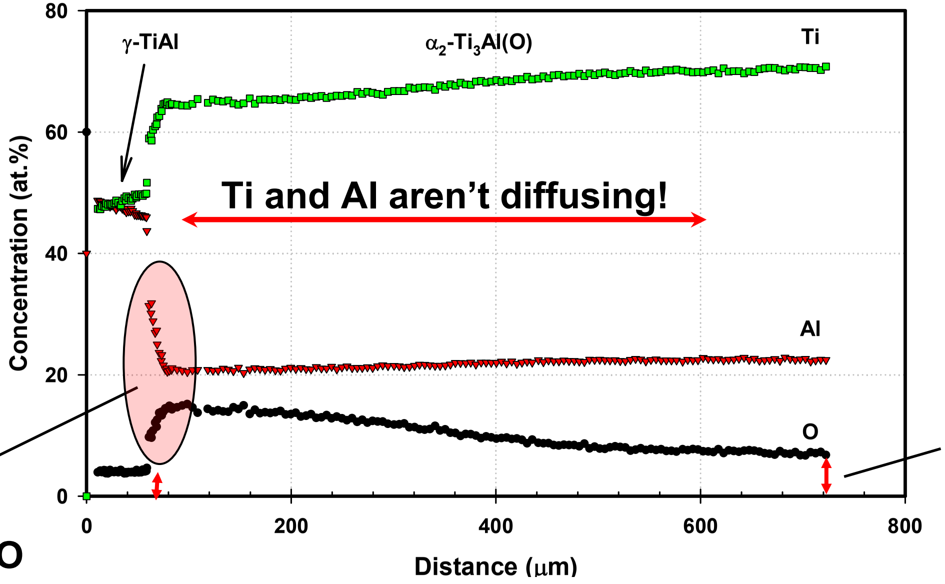
C. Jones, B. Lukley , E. Copland, Intermetallics, **14**, (2006), p. 54.

concentration profiles

Al_2O_3 / Ti-25Al

T = 1100°C, 250 h

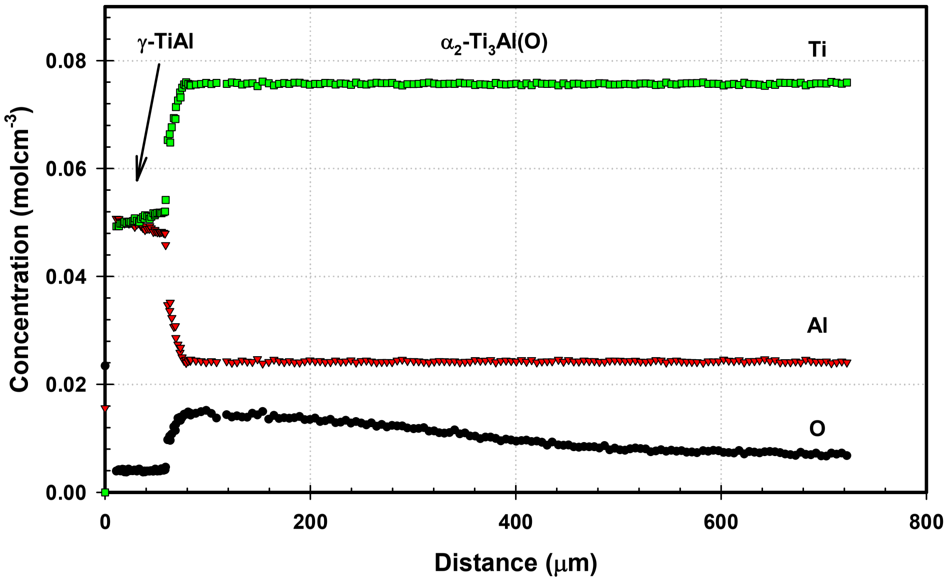
raw EPMA data



"up-hill" diffusion of O

EPMA error, TiO_2-layer

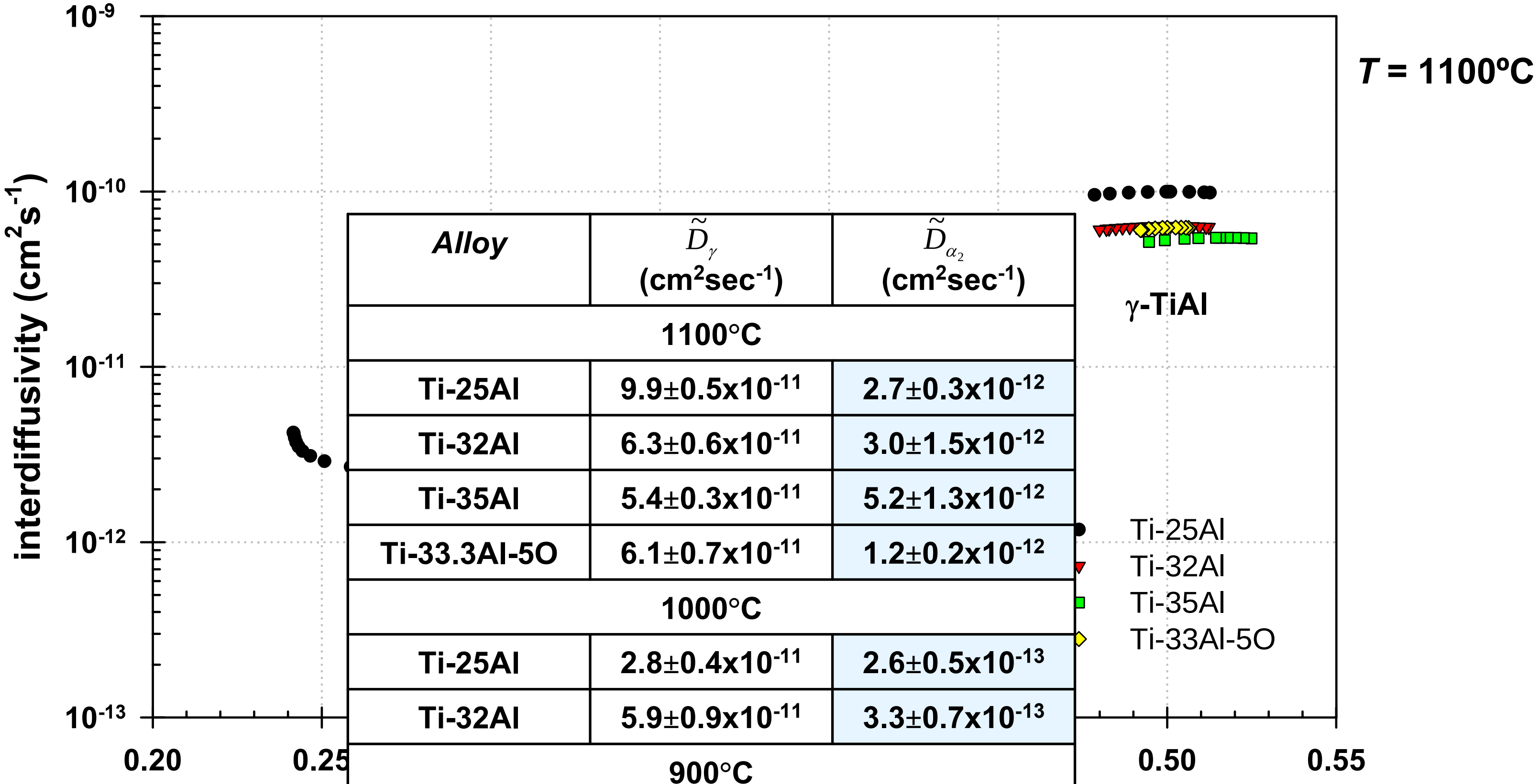
corrected profile



$$C_{\mathrm{i}} = \left(N_{\mathrm{i}} / \left(N_{\mathrm{Ti}} + N_{\mathrm{Al}}\right)\right) / V_m$$

$$C_{\mathrm{O}} = N_{\mathrm{O}} / V_m$$

$\tilde{D}(N_i)$ in α_2-Ti_3Al and γ-TiAl

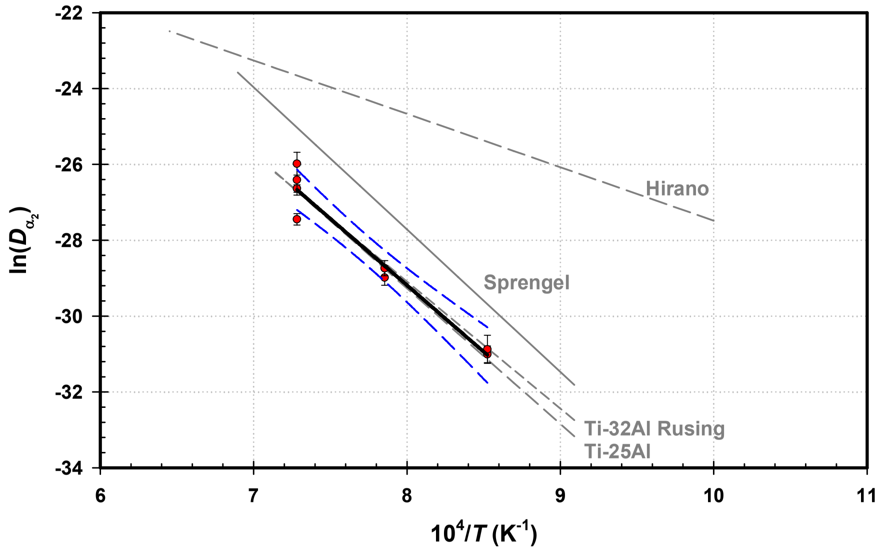


Alloy	$\tilde{D}_\gamma$ (cm^{2}sec^{-1})	$\tilde{D}_{\alpha_2}$ (cm^{2}sec^{-1})
1100°C		
Ti-25Al	$9.9 \pm 0.5 \times 10^{-11}$	$2.7 \pm 0.3 \times 10^{-12}$
Ti-32Al	$6.3 \pm 0.6 \times 10^{-11}$	$3.0 \pm 1.5 \times 10^{-12}$
Ti-35Al	$5.4 \pm 0.3 \times 10^{-11}$	$5.2 \pm 1.3 \times 10^{-12}$
Ti-33.3Al-5O	$6.1 \pm 0.7 \times 10^{-11}$	$1.2 \pm 0.2 \times 10^{-12}$
1000°C		
Ti-25Al	$2.8 \pm 0.4 \times 10^{-11}$	$2.6 \pm 0.5 \times 10^{-13}$
Ti-32Al	$5.9 \pm 0.9 \times 10^{-11}$	$3.3 \pm 0.7 \times 10^{-13}$
900°C		
Ti-25Al	$5.1 \pm 2.0 \times 10^{-12}$	$3.4 \pm 0.9 \times 10^{-14}$
Ti-32Al	$1.4 \pm 0.5 \times 10^{-11}$	$3.9 \pm 1.0 \times 10^{-14}$

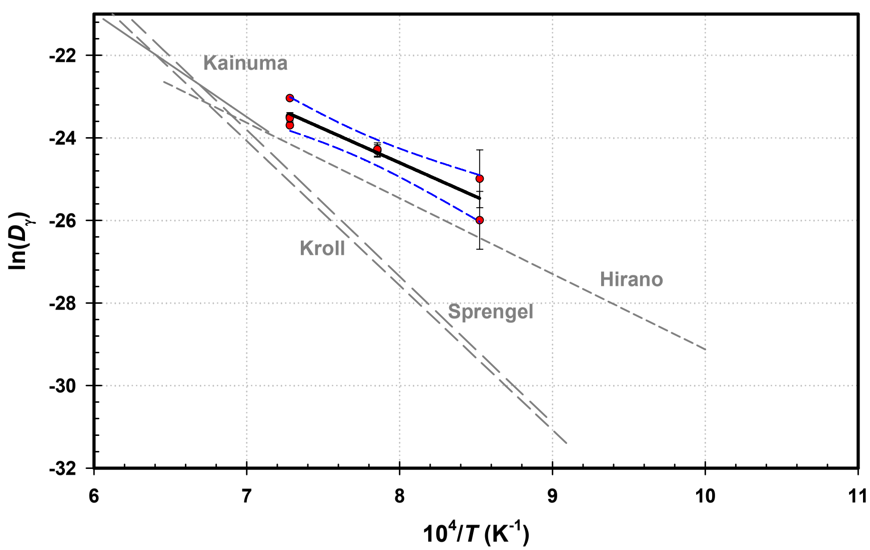
average values

Arrhenius behavior / comparison

α_2-Ti_3Al



γ-TiAl



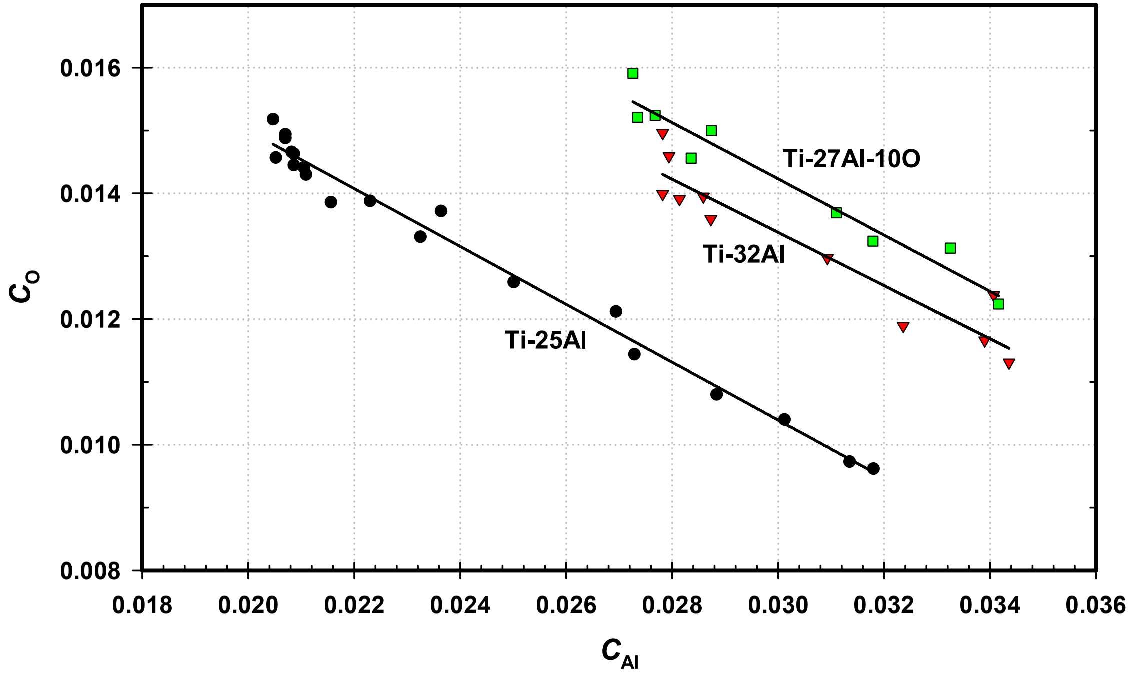
T (°C)	α_2		γ		Method	Reference
	D_O (cm^2s^{-1})	E_a ($kJmol^{-1}$)	D_O (cm^2s^{-1})	E_a ($kJmol^{-1}$)		
1169-1366	-	-	3.0×10^{-3}	210	concentration	Kainuma, Inden (1997)
845-1310	10	312±6	2.8	295±10	concentration	Sprengel (1996)
881-1400	-	-	1.5	291±10	tracer	Kroll, (1992)
897-995	0.3	290±15	-	-	tracer	Rüsing, Herzig (1995)
897-995	n/a	≈350	-	-	concentration	Rüsing, Herzig (1995)
750-1250	1.5×10^{-6}	117±5	2×10^{-5}	152±2	concentration	Hirano, Iijima (1984)
900-1100	0.3	290±25	1.1×10^{-5}	140±40	concentration	Present results

interstitial diffusion of O in α_2-Ti_3Al

- $\tilde{J}_O >> \tilde{J}_{(Al,Ti)}$… “transient equilibrium” (Kirkaldy *et al.* 1958-64)
  O, local equilibrium; redistributes with Ti-Al substitutional lattice

$$\tilde{J}_O^{\,i} = -\tilde{D}_{OO}^{Ti}\frac{\partial C_O}{\partial x} - \tilde{D}_{OAl}^{Ti}\frac{\partial C_{Al}}{\partial x} \cong 0$$

- predict interdiffusion coefficient ratio: $\dfrac{\tilde{D}_{OAl}^{Ti}}{\tilde{D}_{OO}^{Ti}} = -\dfrac{\Delta C_O}{\Delta C_{Al}}$



T = 1100ºC

$\tilde{D}_{OAl} / \tilde{D}_{OO}$ = 0.44±0.08

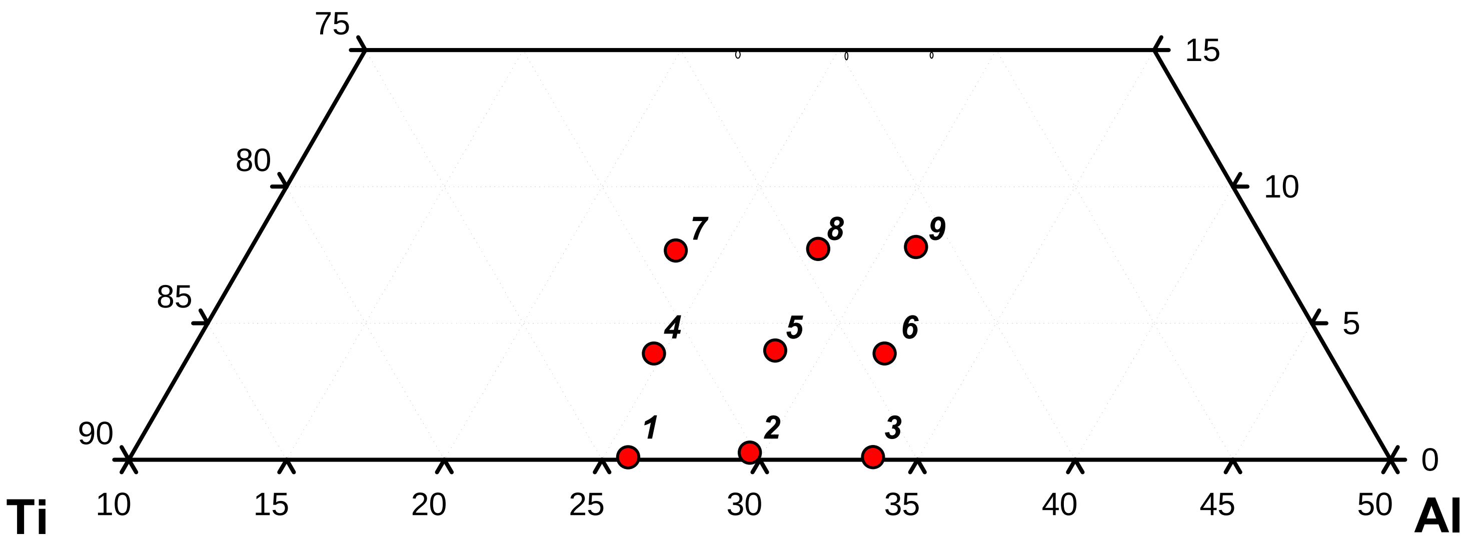
calculated $\tilde{D}_{OO}$

- $\tilde{J}_{O}^{i} = -\tilde{D}_{OO}^{Ti} \frac{\partial C_{O}}{\partial x} - \tilde{D}_{OAl}^{Ti} \frac{\partial C_{Al}}{\partial x}$, **no intersecting diffusion paths…**
- **region of pure O enrichment,** $\frac{\partial C_{Al}}{\partial x} = 0 \quad \rightarrow \quad \tilde{J}_{O}^{i} = -\tilde{D}_{OO}^{Ti} \frac{\partial C_{O}}{\partial x}$
- **EPMA and micro-hardness; assume $\tilde{D}_{OO}$ const.** $\frac{C(x,t) - C_s}{C_O - C_s} = erf\left(\frac{x}{2\sqrt{Dt}}\right)$

Alloy	$\tilde{D}_{OO}^{Ti}$ (10^{-10}cm^{2}s^{-1})			Arrehenius Behaviour	
	1100°C	1000°C	900°C	D_O (cm^{2}s^{-1})	E_a (kJmole^{-1})
I(Ti-25Al)	4.0±1.0	0.75±0.15	0.2±0.1	0.014	200±23
II(Ti-32Al)	5.5±1.5	0.6±0.15	0.15±0.1	0.60	240±37
III(Ti-35Al)	6.5±1.5	1.0±1.5	0.15±0.1	2.37	252±10

$$\tilde{D}_{OO} / \tilde{D}_{Al} = 100 \sim 1000$$

single-phase α_2(O) / α_2(O) couples



alloy	comp. (at.%)
1	Ti-25.8Al-0.1O
2	Ti-29.6Al-0.3O
3	Ti-33.6Al-0.1O
4	Ti-24.7Al-3.9O
5	Ti-28.5Al-4.0O
6	Ti-32.0Al-3.9O
7	Ti-23.5Al-7.7O
8	Ti-28.0Al-7.7O
9	Ti-31.1Al-7.8O

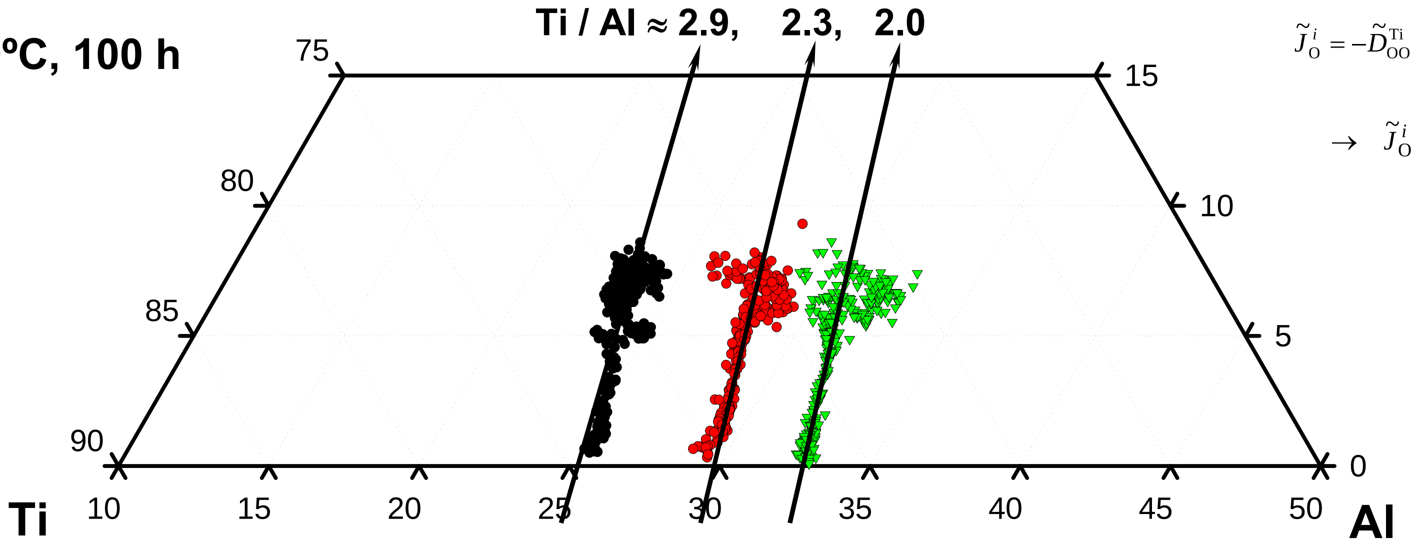
- arc-melted pure-Al, Ti & TiO_2, annealed in closed system:
  - ↳ Ta-foil in SiO_2 capsule
- uni-axial hot press (1100ºC for 2 ~ 4 h); *T* = 1100ºC for 100 h
- analysis: metallography, optical & EPMA
  - ↳ used multi-alloy EPMA standard… TiO_2 surface-layer

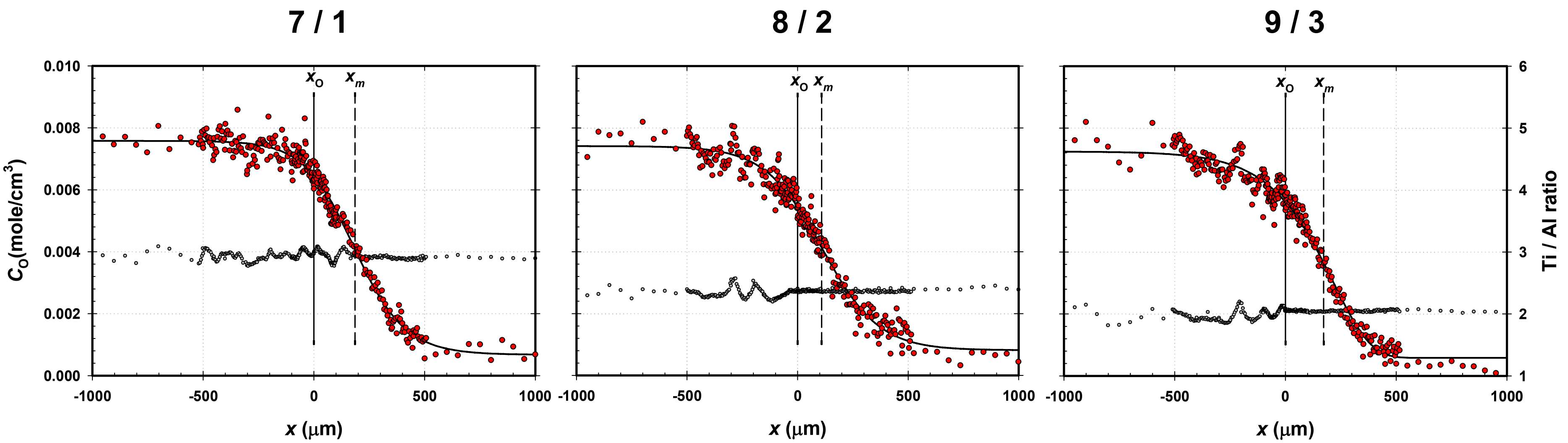
constant Ti / Al ratio

T = 1100°C, 100 h

$$\tilde{J}^{i}_{\mathrm{O}} = -\tilde{D}^{\mathrm{Ti}}_{\mathrm{OO}}\frac{\partial C_{\mathrm{O}}}{\partial x} - \tilde{D}^{\mathrm{Ti}}_{\mathrm{OAl}}\frac{\partial C_{\mathrm{Al}}}{\partial x}$$

$$\rightarrow \quad \tilde{J}^{i}_{\mathrm{O}} = -\tilde{D}^{\mathrm{Ti}}_{\mathrm{OO}}\frac{\partial C_{\mathrm{O}}}{\partial x}$$



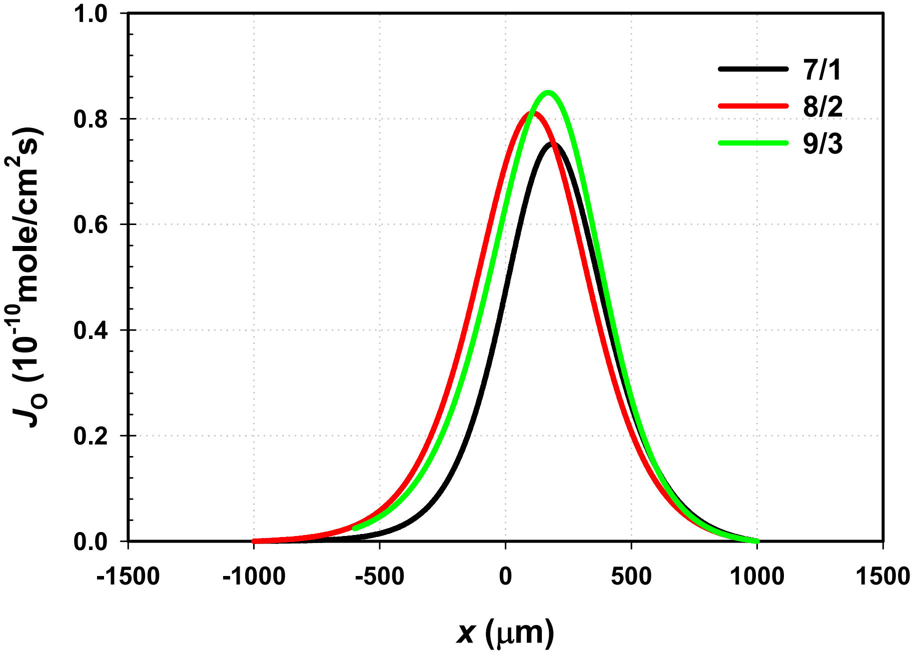


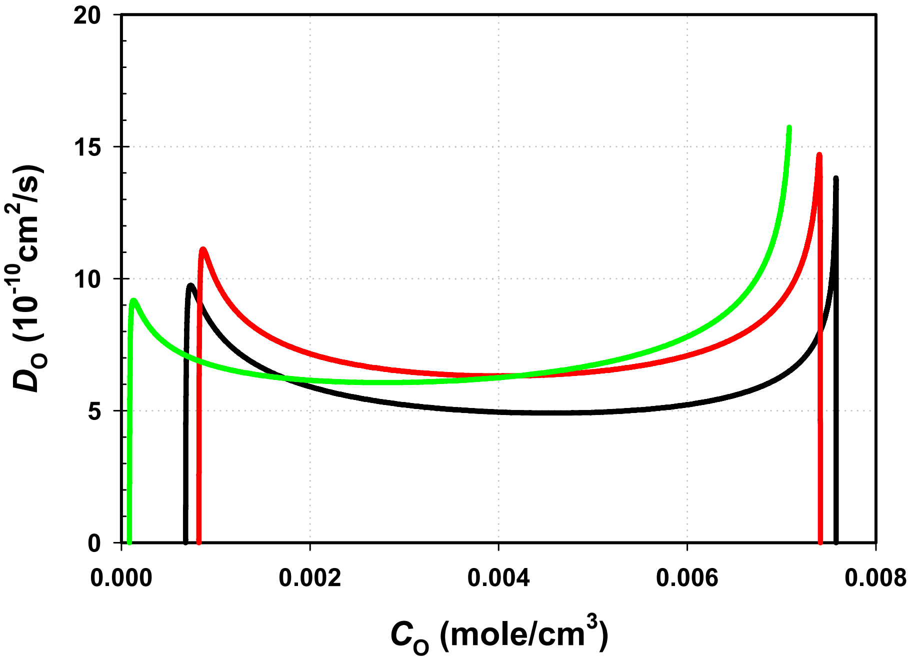
$x_m - x_o$ = 186μm

$x_m - x_o$ = 109μm

$x_m - x_o$ = 173μm

calculated J_O and $\tilde{D}_{OO}$



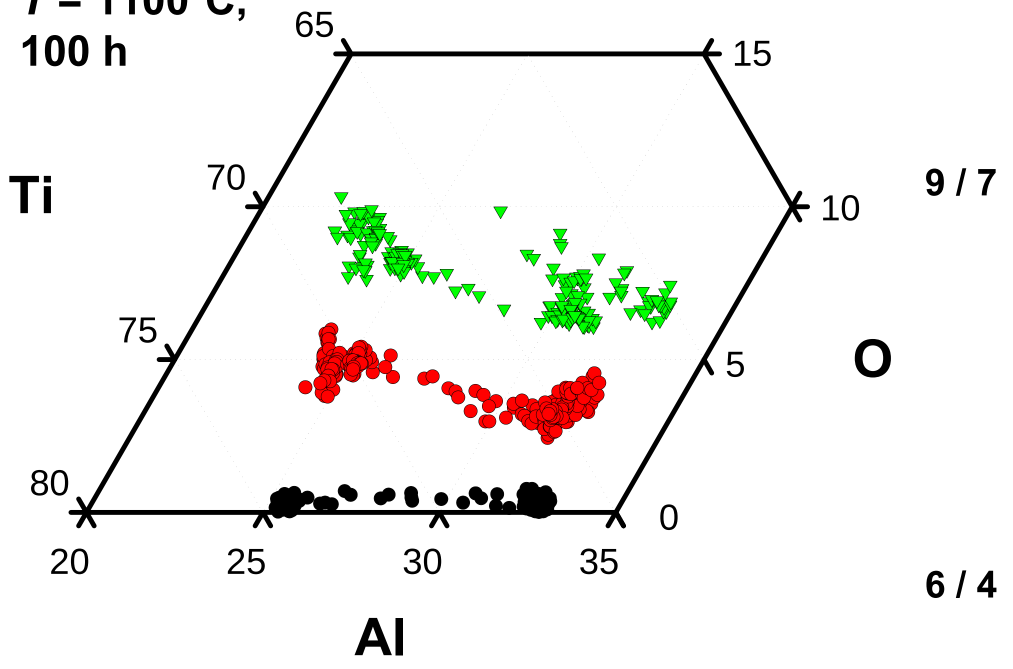


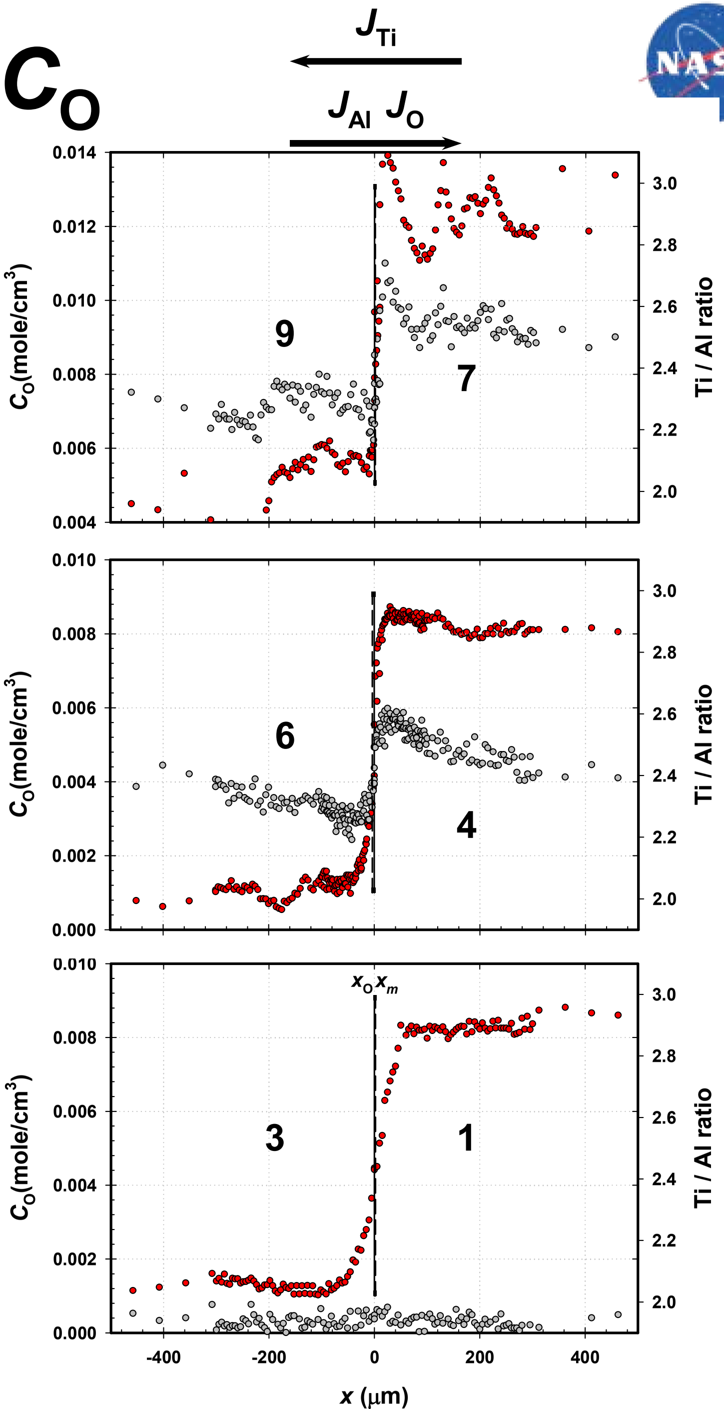
	Ti-Al / Al_2O_3 couples		α_2(O) / α_2(O) couples
alloy	$\tilde{D}_{OO}$ (10^{-10}cm^2/s) T = 1100°C	Ti / Al (couple)	$\tilde{D}_{OO}$ (10^{-10}cm^2/s) T = 1100°C
Ti-25Al	4.0±1.0	2.9 (7 / 1)	4.8 ±1.0
Ti-32Al	5.5±1.5	2.3 (8 / 2)	6.2 ±1.5
Ti-35Al	6.5±1.5	2.0 (9 / 3)	6.1 ±2.0

$\tilde{D}_{OO}$ ~ independent of X_O but small Ti / Al dependence (?)

constant C_O

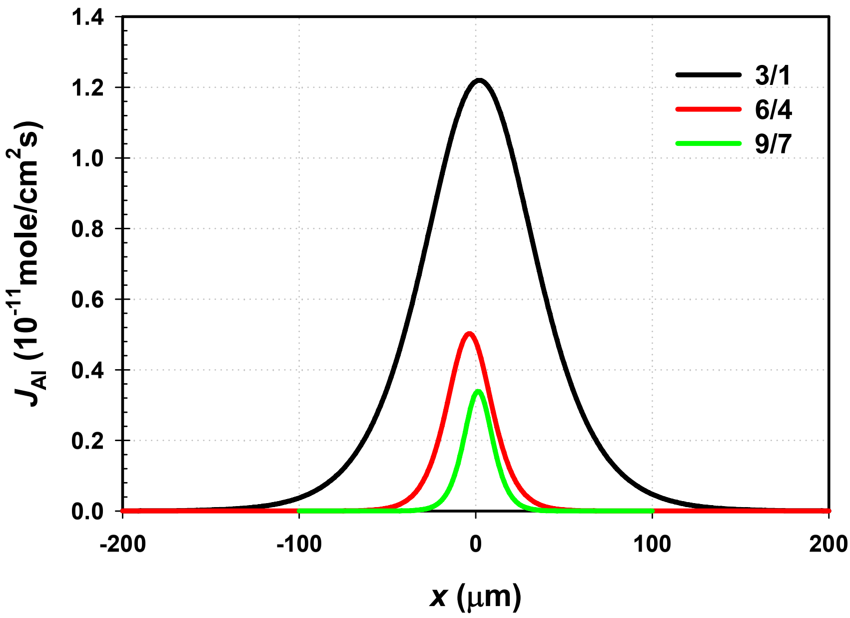
T = 1100ºC,
100 h

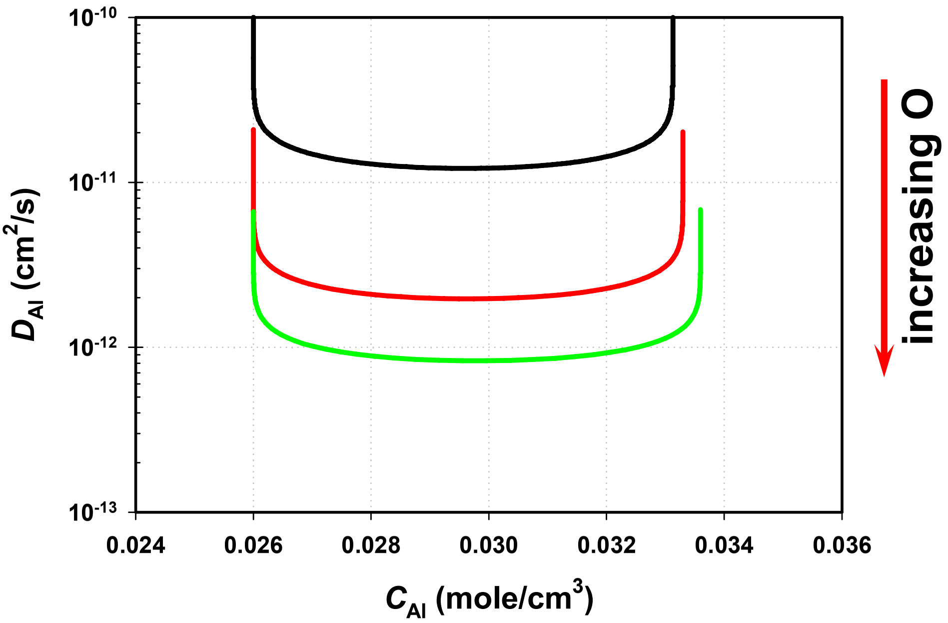


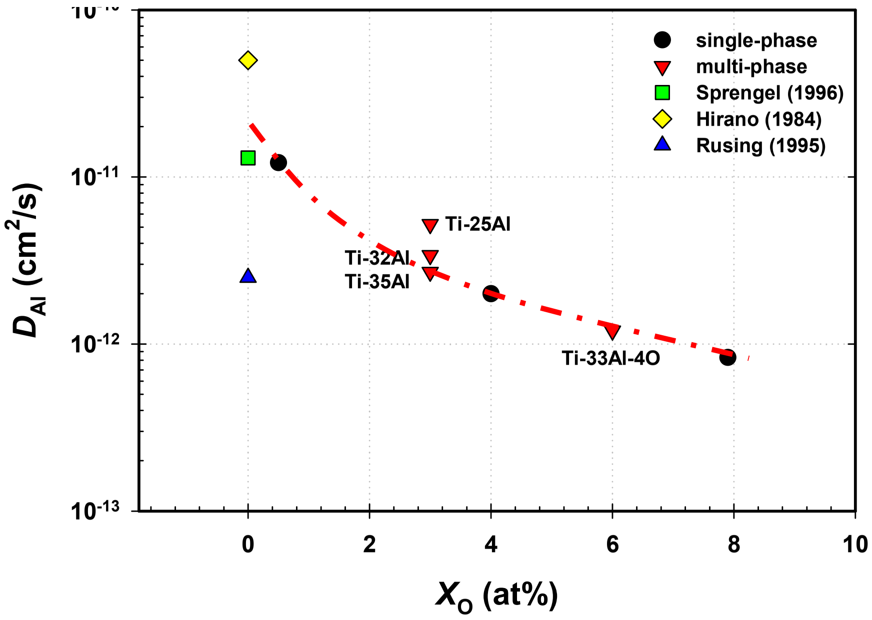


- profiles flipped relative to diffusion path
- classic “up-hill” profile for O…
  - ➥ thermodynamic interaction: Ti-Al → O
- Ti-Al interaction zone decreases with X_O
  - ➥ O → Ti-Al: kinetic / thermodynamic ?
  - ➥ expect similar $\Delta\mu_{(Ti,Al)}$ for each X_O

calculated $\tilde{J}_{Al}$ and $\tilde{D}_{Al}$

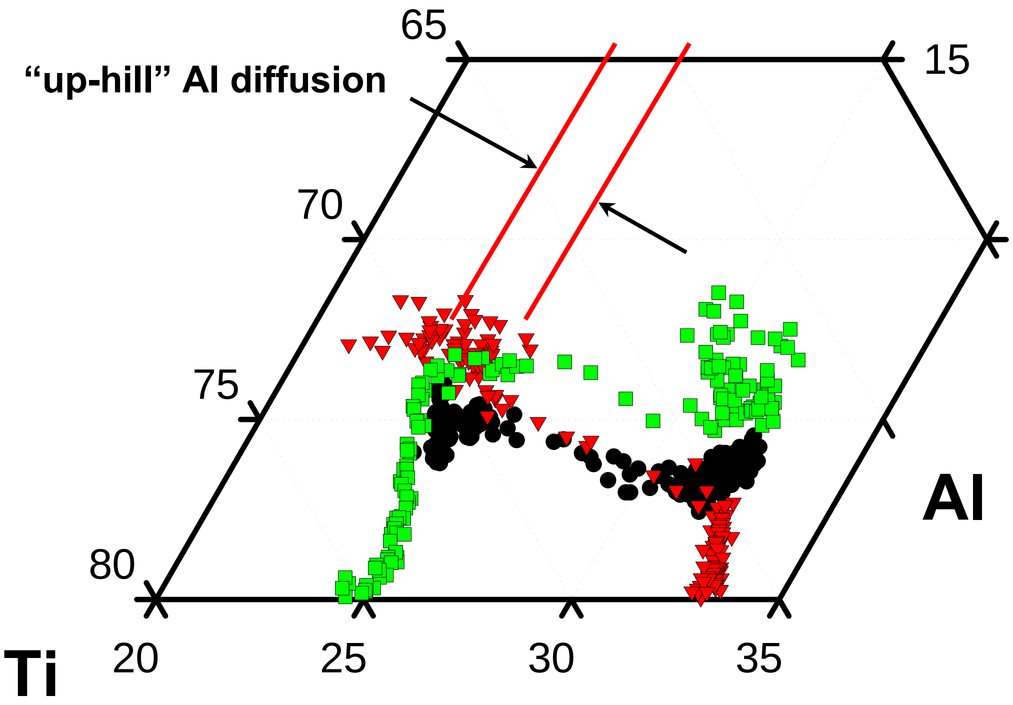






- **Ti-Al and O diffusion isn't independent**
- **X_O not controlled in previous studies:**
  - **Sprengel: SiO_2 capsules, no Ta-foil**
  - **Rusing: flowing Ar-atmosphere**

“intersecting” paths: 9-1, 7-3, 6-4

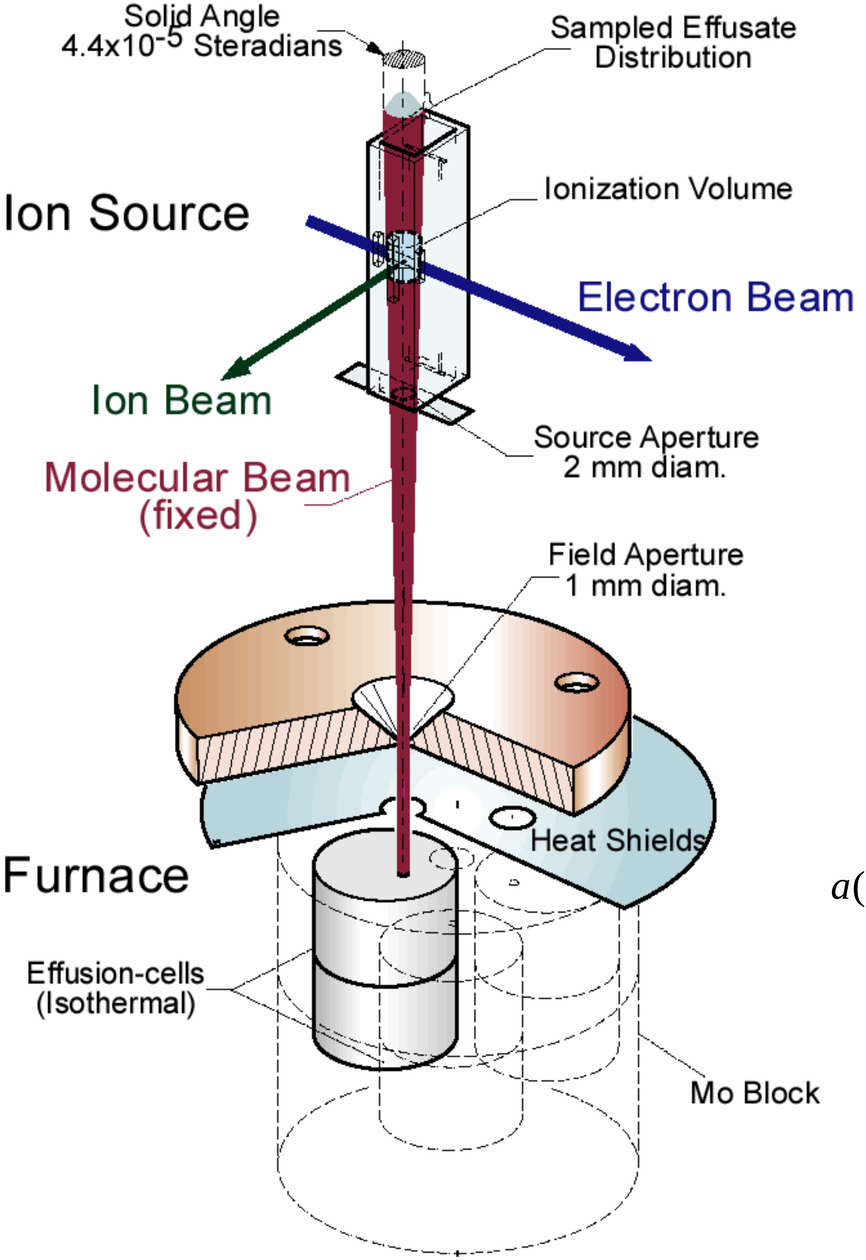


$$\tilde{J}_{\mathrm{O}}^{i} = -\tilde{D}_{\mathrm{OO}}^{\mathrm{Ti}} \frac{\partial C_{\mathrm{O}}}{\partial x} - \tilde{D}_{\mathrm{OAl}}^{\mathrm{Ti}} \frac{\partial C_{\mathrm{Al}}}{\partial x}$$

$$\tilde{J}_{\mathrm{Al}}^{i} = -\tilde{D}_{\mathrm{AlO}}^{\mathrm{Ti}} \frac{\partial C_{\mathrm{O}}}{\partial x} - \tilde{D}_{\mathrm{AlAl}}^{\mathrm{Ti}} \frac{\partial C_{\mathrm{Al}}}{\partial x}$$

- **9-1 and 7-3 don’t intersect; 7-3 and 6-4 are parallel…**
  - ➥ **new couples needed to determine kinetic interaction O → Ti-Al**
- **9-1 diffusion path shows “up-hill” Al diffusion:**
  - ➥ **O dissolution must: increase *a*(Al), decrease *a*(Ti) (or both)**

thermodynamic measurements



multi-cell *KEMS*

pressure measurement

$$p(\mathrm{i}) = I_{ik}^{+} T \big/ S_{ik}$$

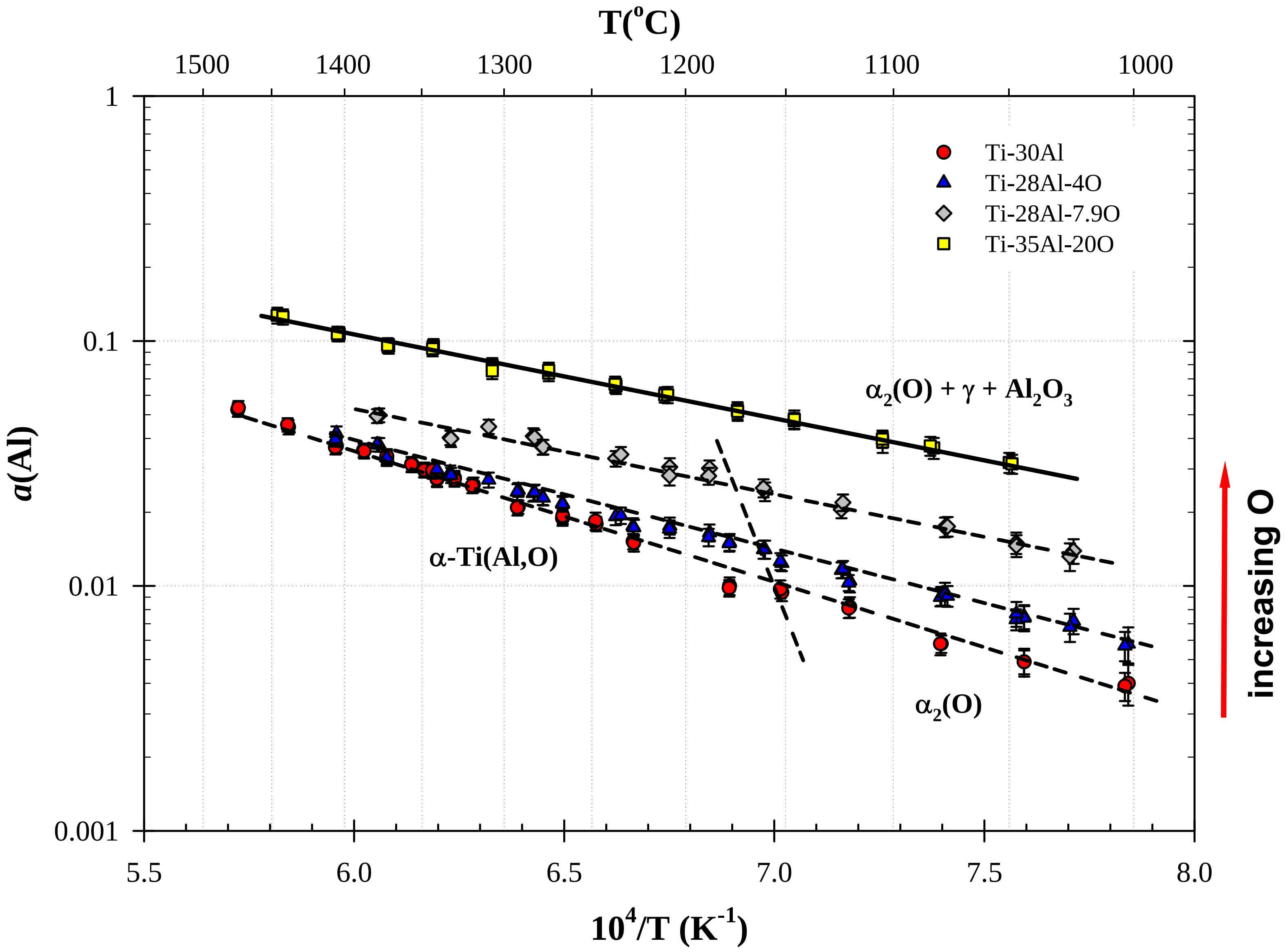
activity measurement

$$a(\mathrm{i}) = \frac{p(\mathrm{i})}{p^{o}(\mathrm{i})} = \frac{I_\mathrm{i}}{I_\mathrm{i}^{o}}$$

$$a(\mathrm{i}) = \frac{p(\mathrm{i})}{\cancel{p^{\circ}(\mathrm{Au})}} \cdot \left[\frac{\cancel{p^{\circ}(\mathrm{Au})}}{p^{\circ}(\mathrm{i})}\right] = \frac{I_\mathrm{i}}{I_\mathrm{Au}^{\circ}} \cdot \boxed{\frac{\mathrm{S_{Au}}}{\mathrm{S_i}}} \cdot \frac{g(R)}{g(A)} \cdot \boxed{\left[\frac{p^{\circ}(\mathrm{Au})}{p^{\circ}(\mathrm{i})}\right]}$$

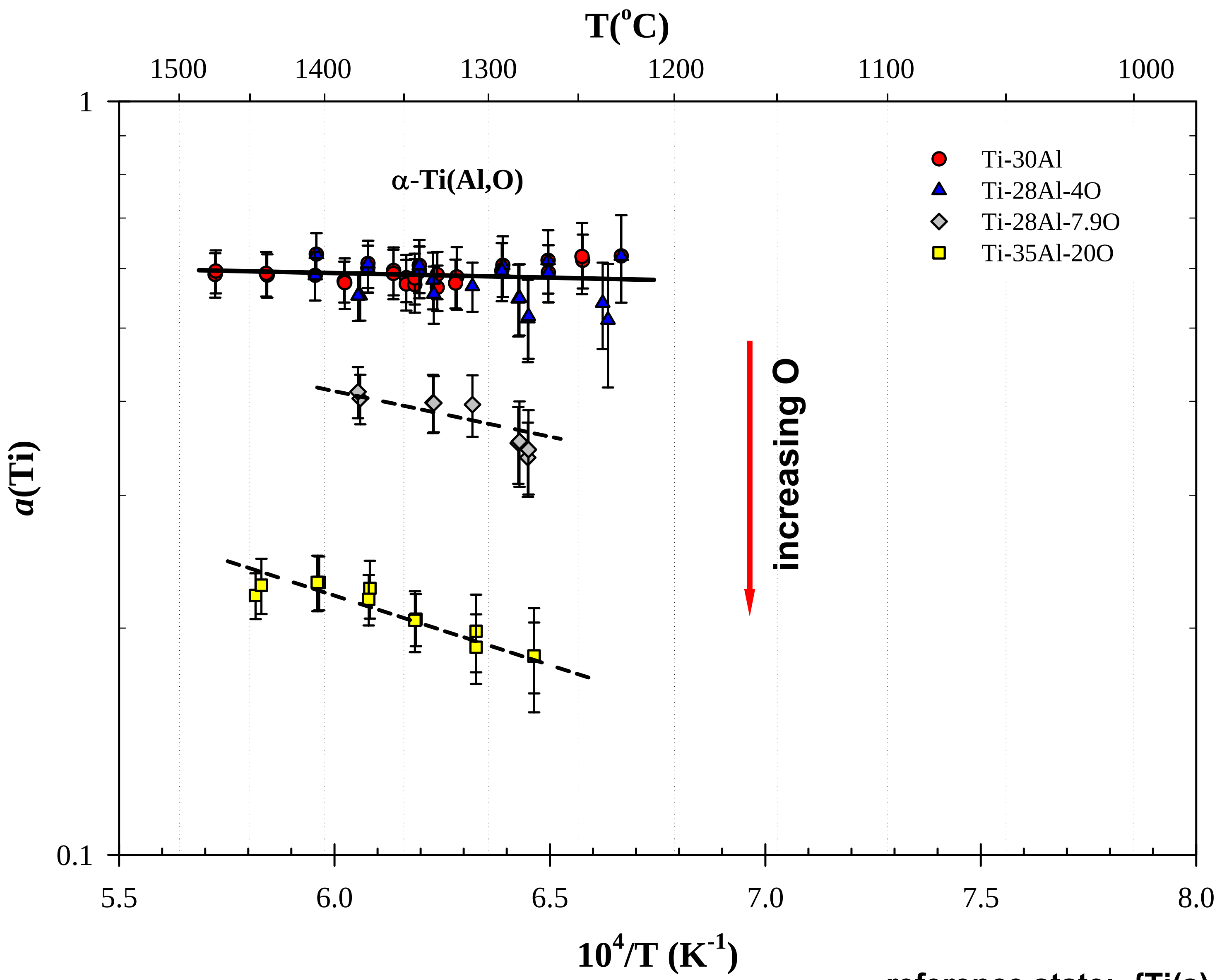
(i = Ti, Al, Al_2O)

$a(Al)$ vs. X_O



reference state: $\{Al(l) + Al_2O_3(s)\}$

a(Ti) vs. X_O



reference state: {Ti(s) + Y_2O_3(s)}

summary

- α_2 / Al_2O_3 and α_2(O) / α_2(O) couples… Ti-Al-O reaction behavior
- unsaturated α_2(O) reduces Al_2O_3: γ-layer, “up-hill” $\tilde{J}_O$ in α_2(O)
- $\tilde{J}_O >> \tilde{J}_{Al}$; treat subst. and interstitial lattices independently
  - ↪ Ti-Al “pseudo binary” $\tilde{D} = \tilde{D}(C_i)$, scatter in data (effect of X_O)
  - ↪ “transient equ.”: $\tilde{D}_{OAl}$ / $\tilde{D}_{OO}$ and $\tilde{D}_{OO}$, slight Ti / Al dependence
- α_2(O) / α_2(O) couples: confirm $\tilde{D}_{OAl}$ / $\tilde{D}_{OO}$ and $\tilde{D}_{OO}$ behavior, but Ti-Al interdiffusion reduced > 10x with X_O 0.005 → 0.08
  - ↪ thermodynamic interaction + change in mobility (?)
  - ↪ difficult to observe kinetic aspect; thermodynamics is clear
- more work is need…
  - ↪ significant insight to oxidation of Ti-Al alloys

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