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Oxygen sources and control in titanium PIM process

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Oxygen Sources and Control in Titanium PIM Process

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MIM2010
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Oxygen sources and control in P/M

- NRC-IMI Powder Forming
- Titanium Interstitials Control
- Sources of Oxygen in P/M
- Specific examples



The diagram shows a central core of 'Carbides', 'Metal', and 'Ceramic' particles. This core is surrounded by a ring of processes: 'Modelling', 'Prototyping', 'Debinding', 'Lubricant', 'Additive', 'Consolidation', 'Technology transfer', 'Mixing', 'Binder', 'Shaping', and 'Characterization'. Three external circles are connected to the ring: 'Press and Sinter' at the top, 'Injection Molding' at the bottom left, and 'Foam and Porous' at the bottom right.



NRC-IMI Background
Titanium powder forming

Ti-Press and Sinter


Mixing

Uniaxial Pressing

Debinding

Sintering

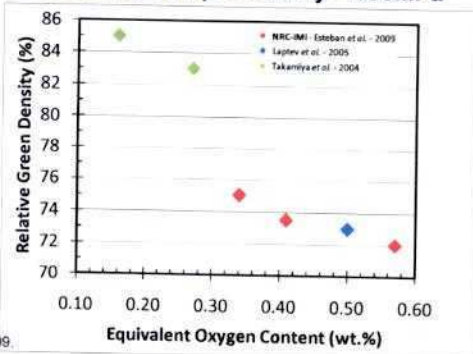
- Powder
- Lubricant
- Master Alloy



$O_{Eq} (\%at) = O + 1.96 \cdot N + 0.52 \cdot C$

Esteban et al, "Study of Compaction and Ejection of Hydrided-Dehydrated Titanium Powder", accepted in Powder Technology, 2009.

Ti Powder Compressibility – 500MPa



Equivalent Oxygen Content (wt.%)	Relative Green Density (%)	Source
0.15	85	Takamiya et al. - 2004
0.25	83	Takamiya et al. - 2004
0.35	75	NRC-IMI - Esteban et al. - 2009
0.40	73	NRC-IMI - Esteban et al. - 2009
0.50	72	Laptev et al. - 2005
0.55	71	NRC-IMI - Esteban et al. - 2009



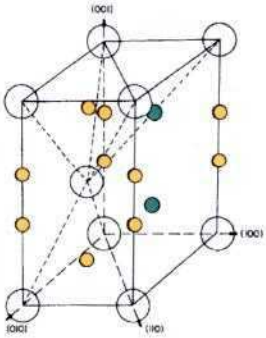
Interstitial Control in Titanium...why?

Standards	Title	O (wt.%)	N (wt.%)	C (wt.%)
ASTM F67 ISO-5832-2	Unalloyed Titanium, for Surgical Implant Applications			
	Grade 1	0.18	0.03	0.08
	Grade 2	0.25	0.03	0.08
	Grade 3	0.35	0.05	0.08
	Grade 4	0.40	0.05	0.08
ASTM-F1472	Wrought Ti-6Al-4V Alloy for Surgical Implant Applications	0.20	0.05	0.08
ASTM F136	Wrought Ti-6Al-4V ELI (Extra Low Interstitial) Alloy for Surgical Implant Applications	0.13	0.05	0.08
ASTM F1580	Titanium Powders for Coatings of Surgical Implants	0.40	0.06	0.10
ASTM B265	Standard Specification for Titanium and Titanium Alloy Strip, Sheet, and Plate (Grade 5)	0.20	0.05	0.10
ASTM B367	Standard Specification for Titanium and Titanium Alloy Castings (Grade 5)	0.25	0.05	0.10
ASTM B817	Standard Specification for Powder Metallurgy (P/M) Titanium Alloy Structural Components (Grade 5)	0.30	0.04	0.10
WK22193	Metal Injection Molded Ti-6Al-4V Net or Near Net Parts for Surgical Implant Applications			

NEW

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Interstitial solubility in α -titanium



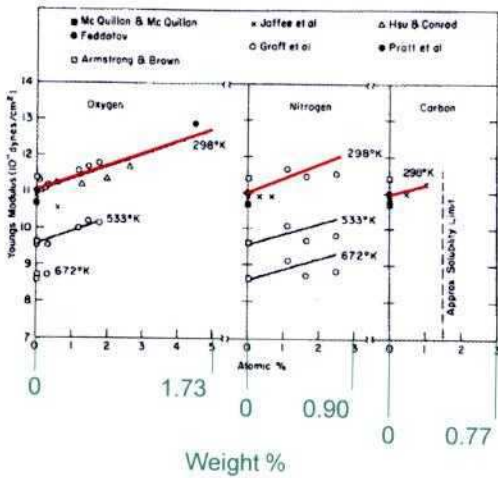
α -Titanium (hcp)	β -Titanium (bcc)
Octahedral sites Diameter : 0.122 nm	
Tetrahedral sites Diameter : 0.066 nm	Tetrahedral sites Diameter : 0.044 nm

Element	Atomic diameter (nm)	Volume expansion nm ³ per at. %	Maximum solubility	
			Atomic %	Weight %
O	0.120	0.00013	30	12.5
N	0.142	0.00018	19	6.4
C	0.154	0.00049	2	0.25

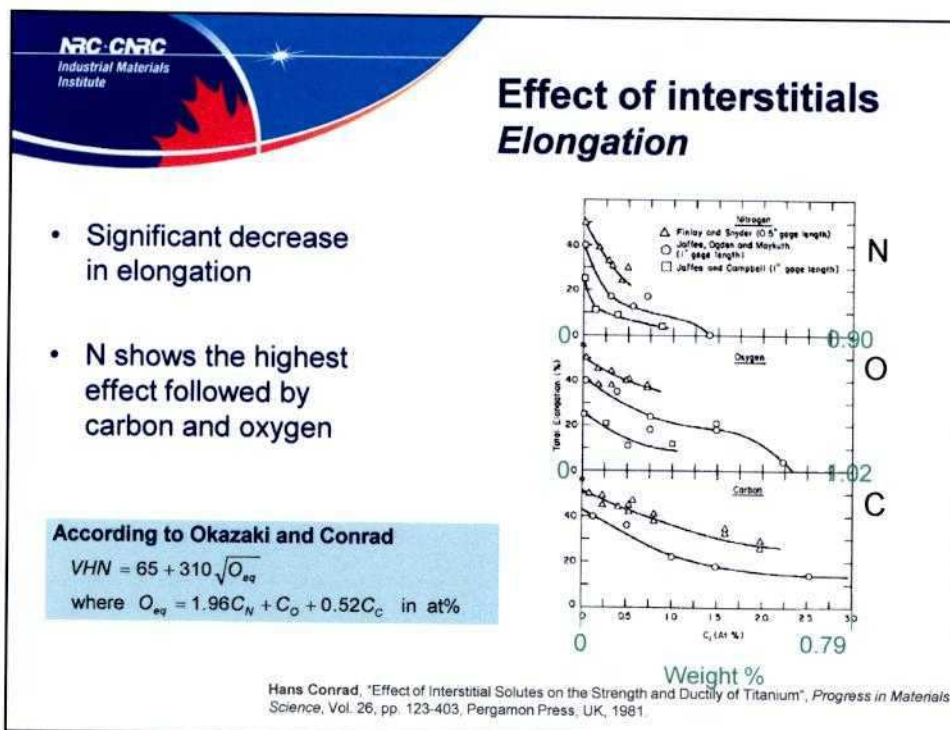
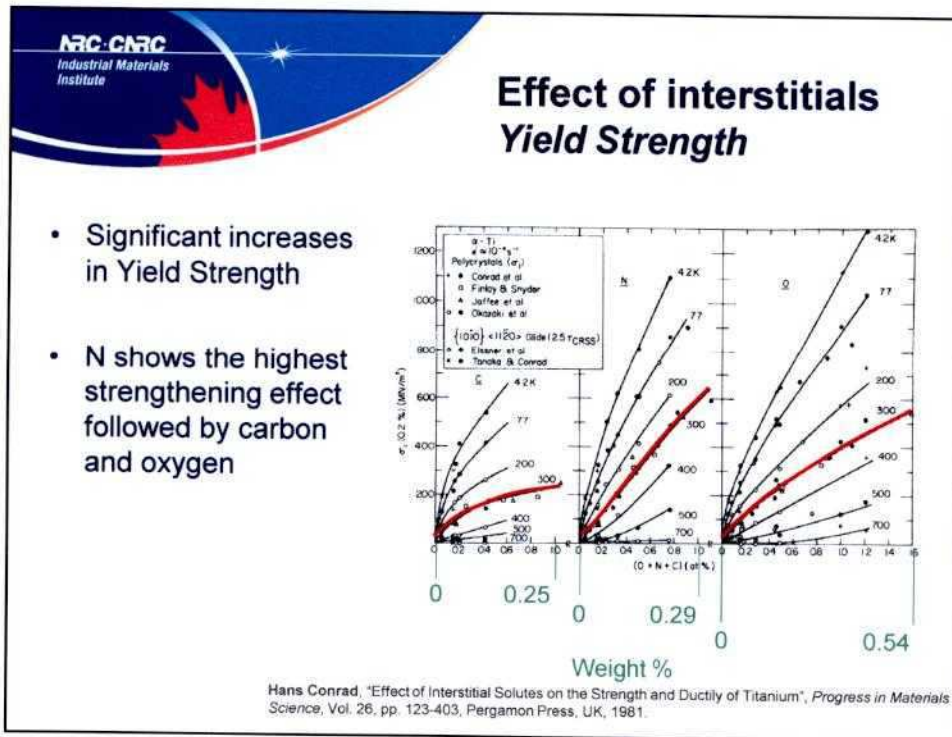
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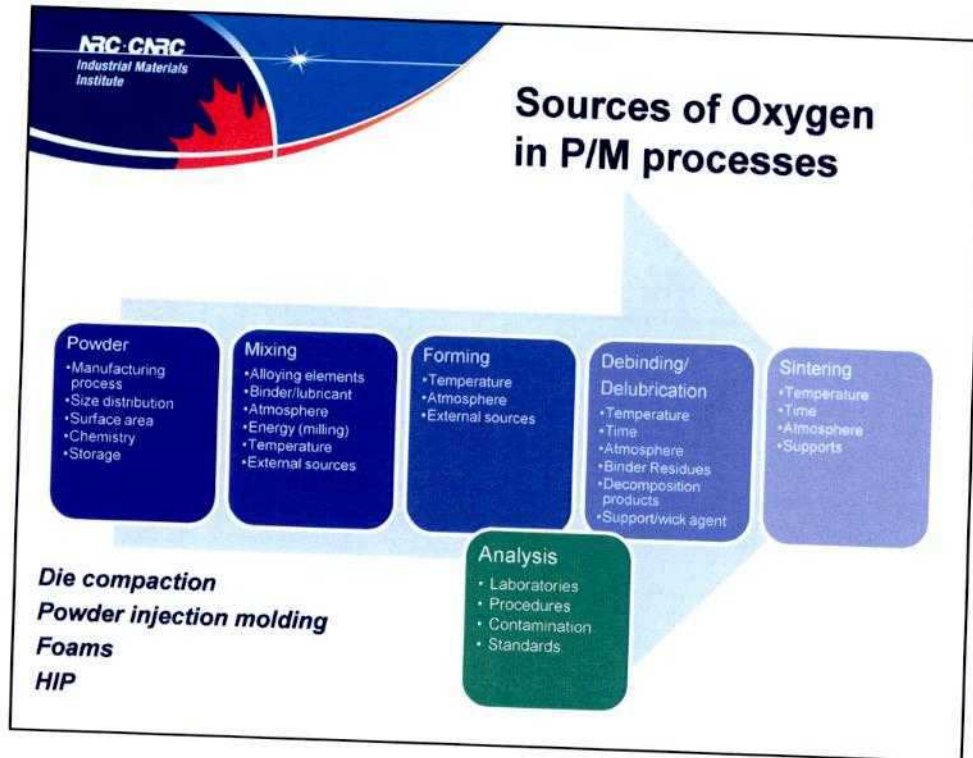
Effect of interstitials *Elastic Modulus*

- Increase of the Young's Modulus with increased interstitial contents
- Similar effects from O, N and C
- Relatively minor effect below 1wt. % of interstitial content



Hans Conrad, "Effect of Interstitial Solutes on the Strength and Ductility of Titanium", *Progress in Materials Science*, Vol. 26, pp. 123-403, Pergamon Press, UK, 1981.





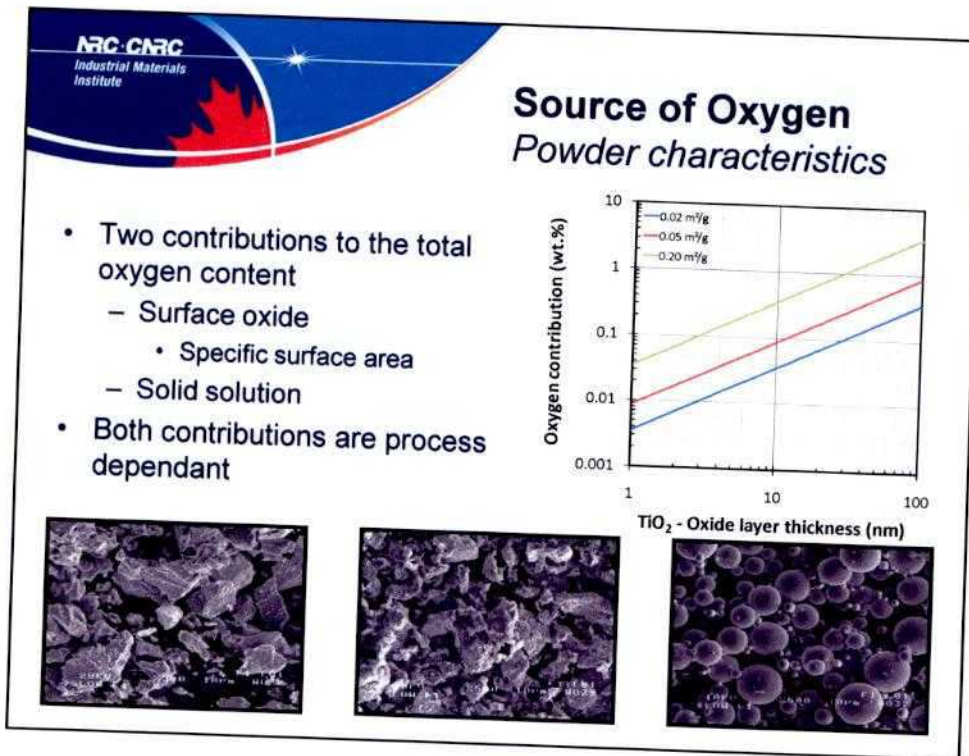
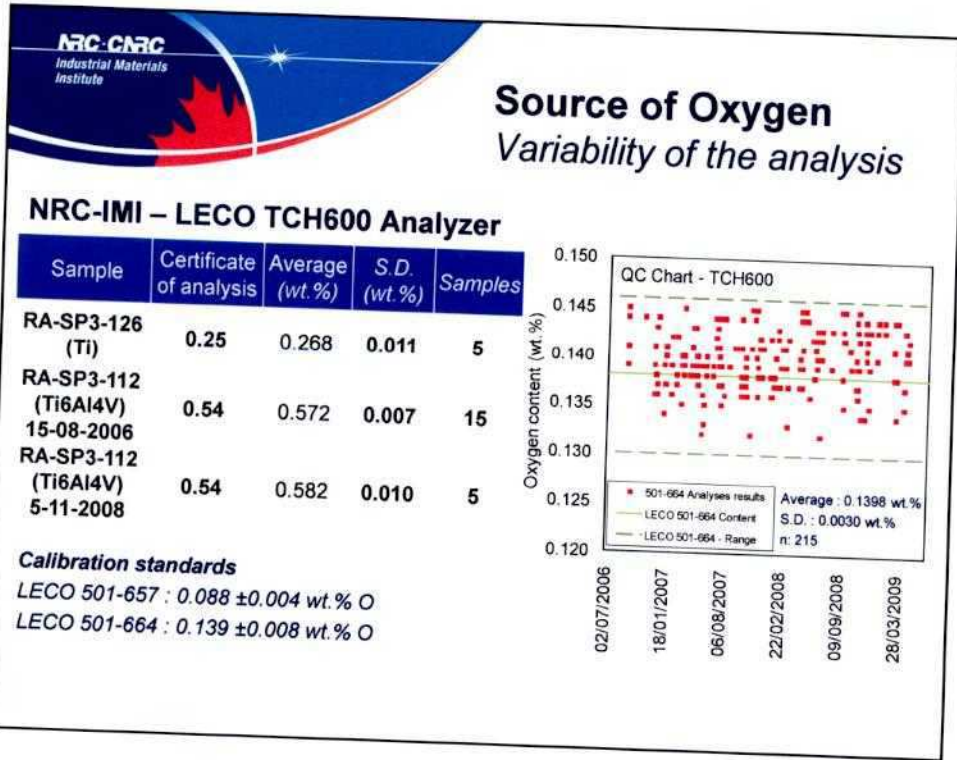
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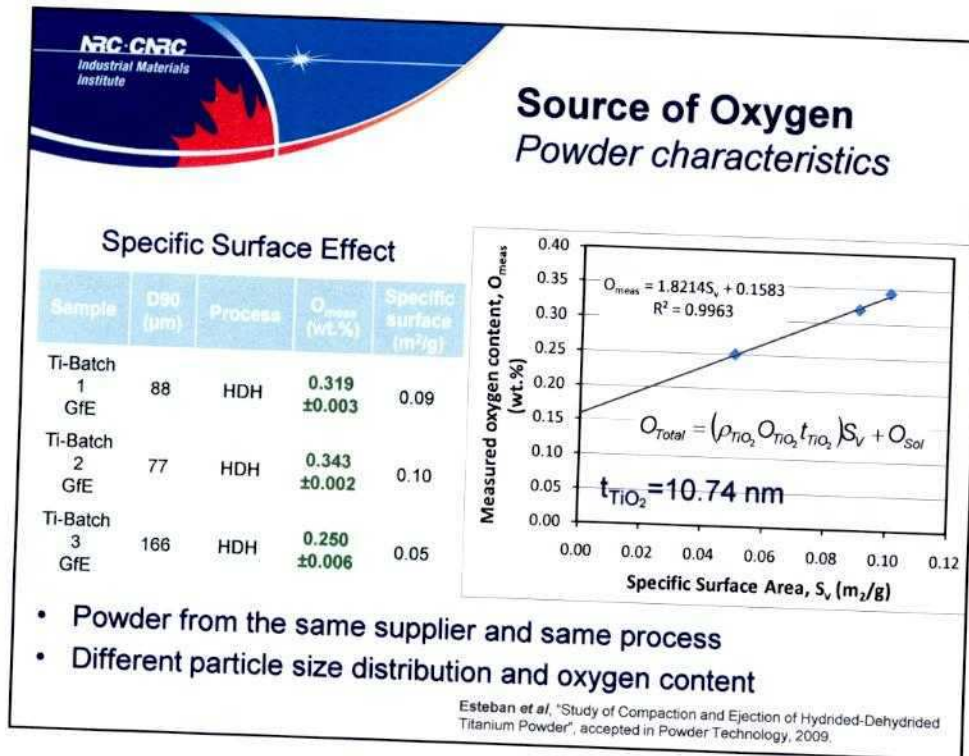
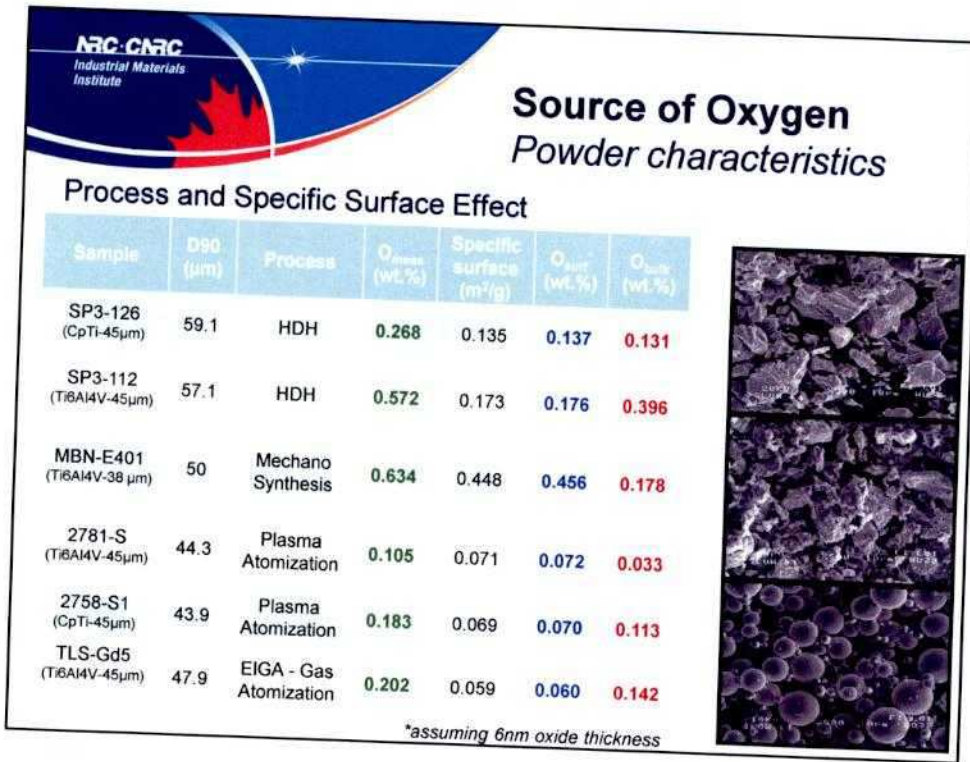
Source of Oxygen Variability of the analysis

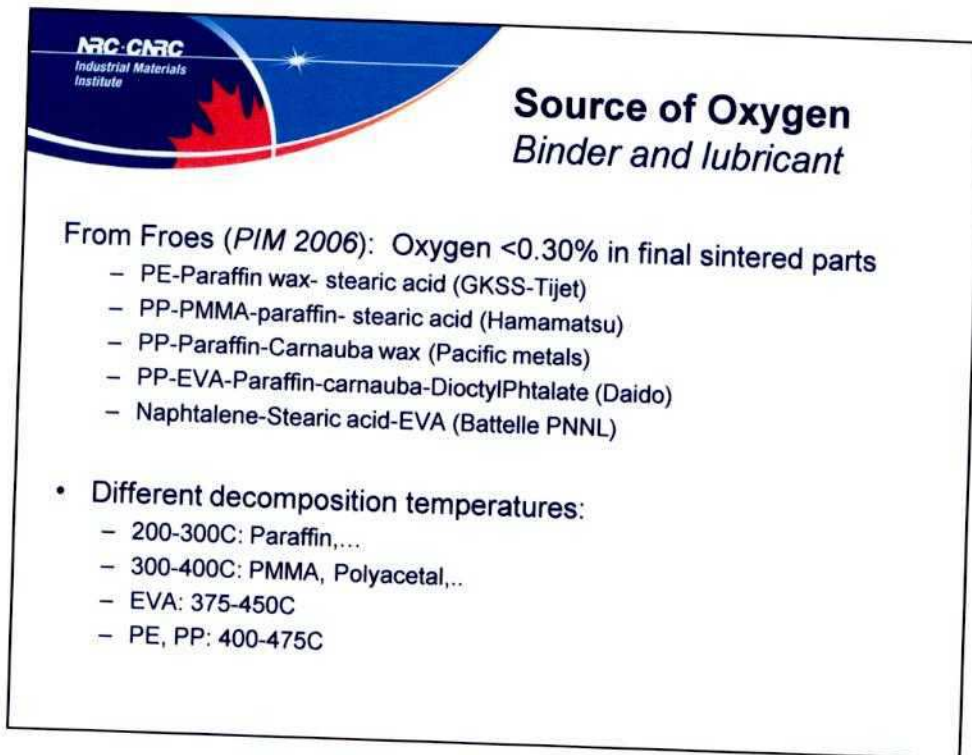
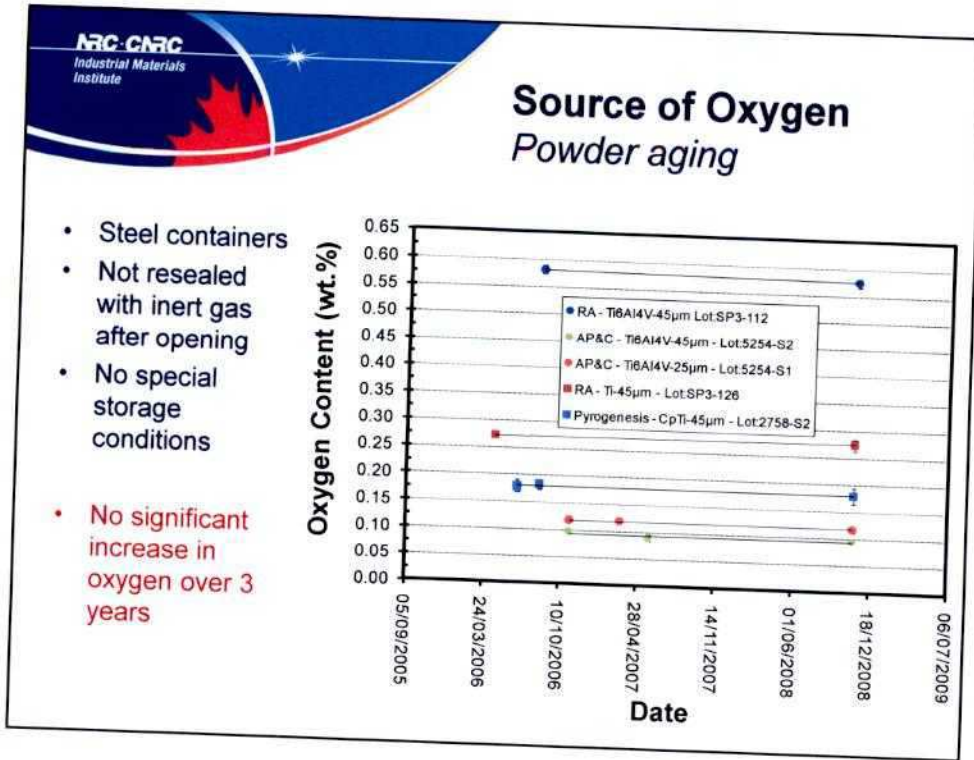
Round robin – HDH -45µm powder
 Certified laboratories serving aerospace and medical sectors
 Expertise with oxygen analysis in castings, forgings, other wrought products
 Oxygen analysis results (wt.%)

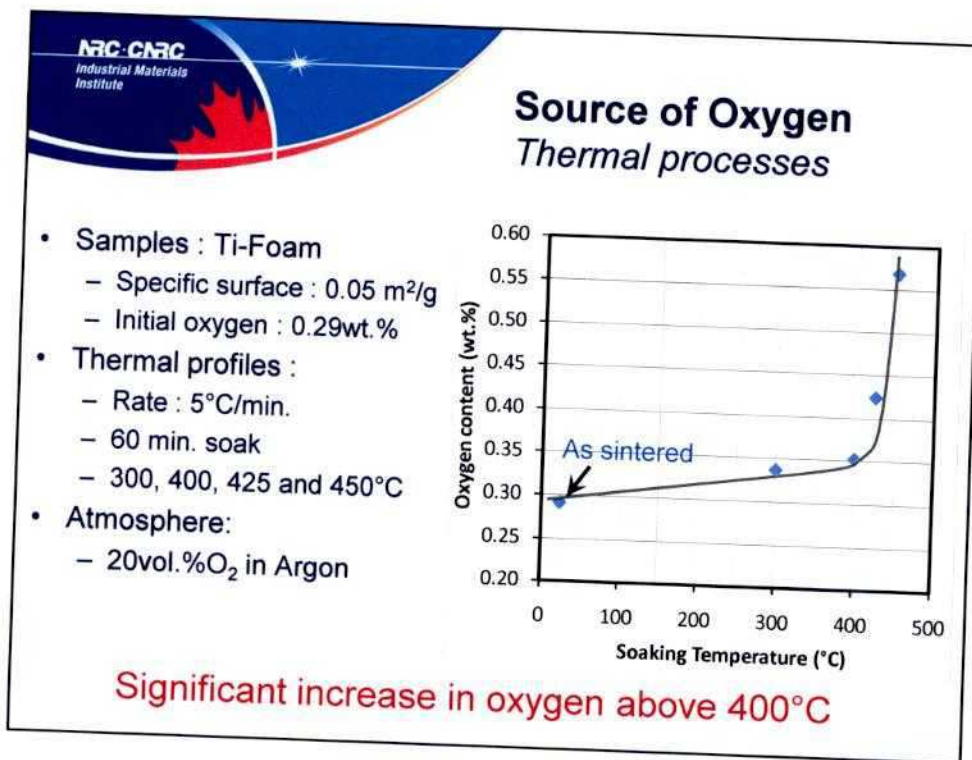
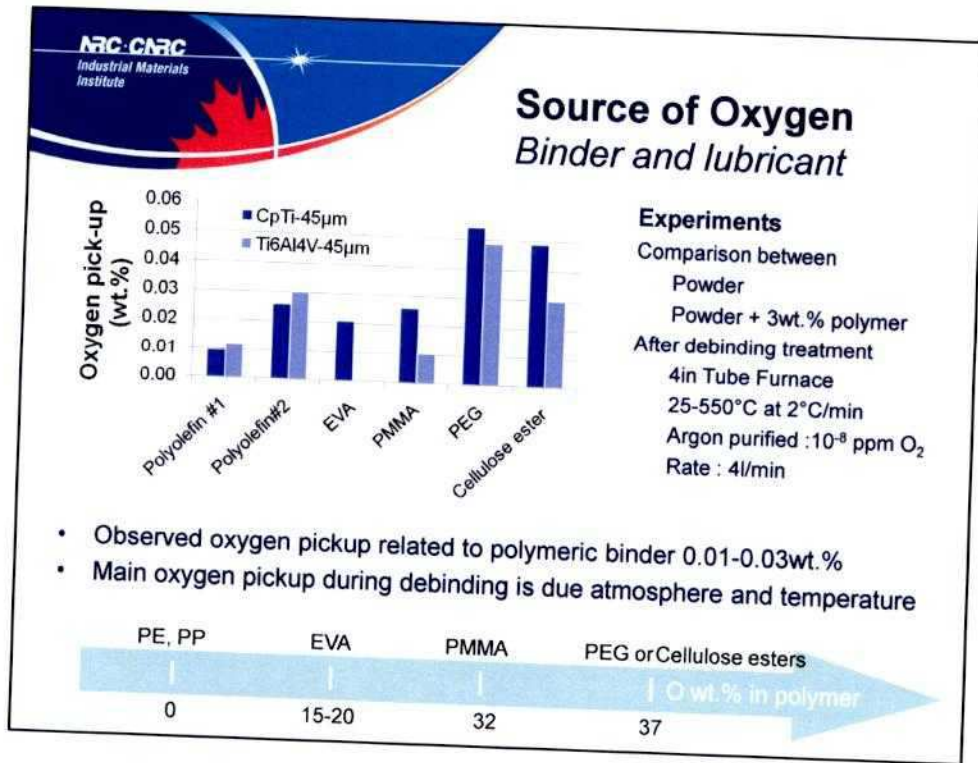
Sample	Certificate of analysis	G	B	S	B2	Supplier	Average Labs	Standard deviation Labs
RA-SP3-126 (Ti)	0.25	0.109	0.63	0.276	0.221	0.26	0.299	0.196
RA-SP3-112 (Ti6Al4V)	0.54	0.22	0.66	0.57	0.503	0.53	0.497	0.166

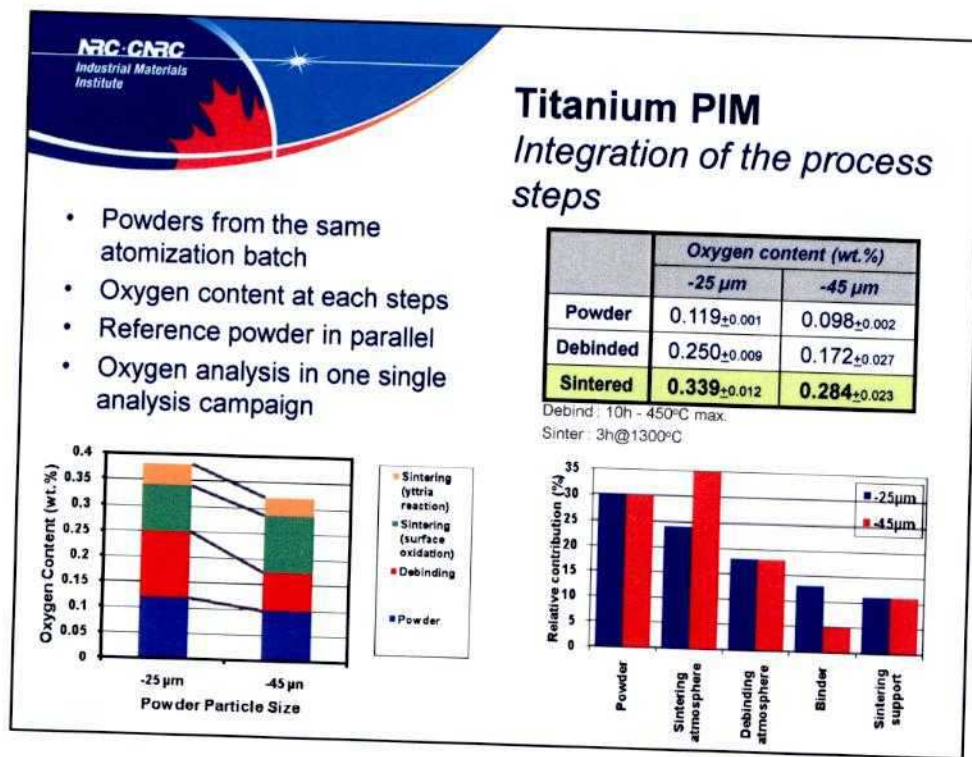
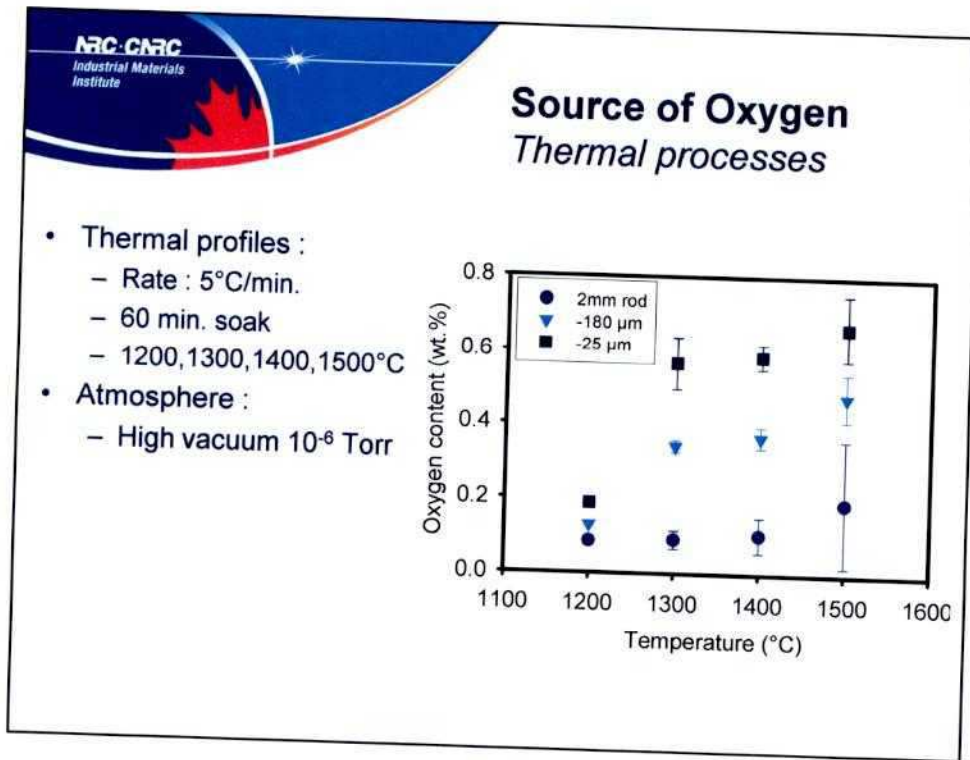
Arrows pointing up from the bottom of the table indicate variability for the G, B, S, B2, and Supplier columns.











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Porous Ti Specific concerns

- In the context of standard and specification development
 - Oxygen content specification = mechanical properties
 - Which oxygen is important? Surface, bulk or both...
 - Porous Ti keeps high surface area during the whole process

The figure includes three micrographs (a, b, and a cross-section) and a line graph. The graph plots the change in oxygen content, $\Delta\%O$ (weight), against the number of cycles (N). The data points show a linear increase from 0.05 wt% at 1 cycle to approximately 0.32 wt% at 6 cycles.

N (number of cycle)	$\Delta\%O$ (weight)
1	0.05
2	0.10
3	0.17
4	0.25
5	0.27
6	0.32

Lefebvre and Baril, "Effect of Oxygen Content and Distribution on the Compression Properties of Titanium Foams", *Advanced Engineering Materials*, vol. 10, no. 9, 868-876, 2008.

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Porous Ti Specific concerns

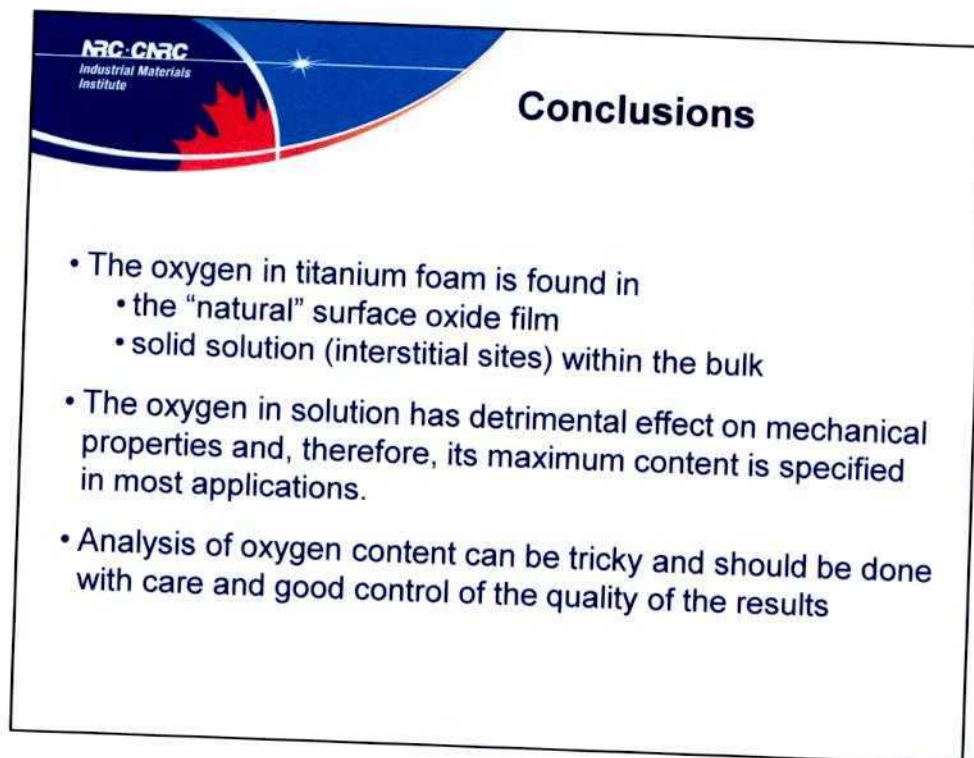
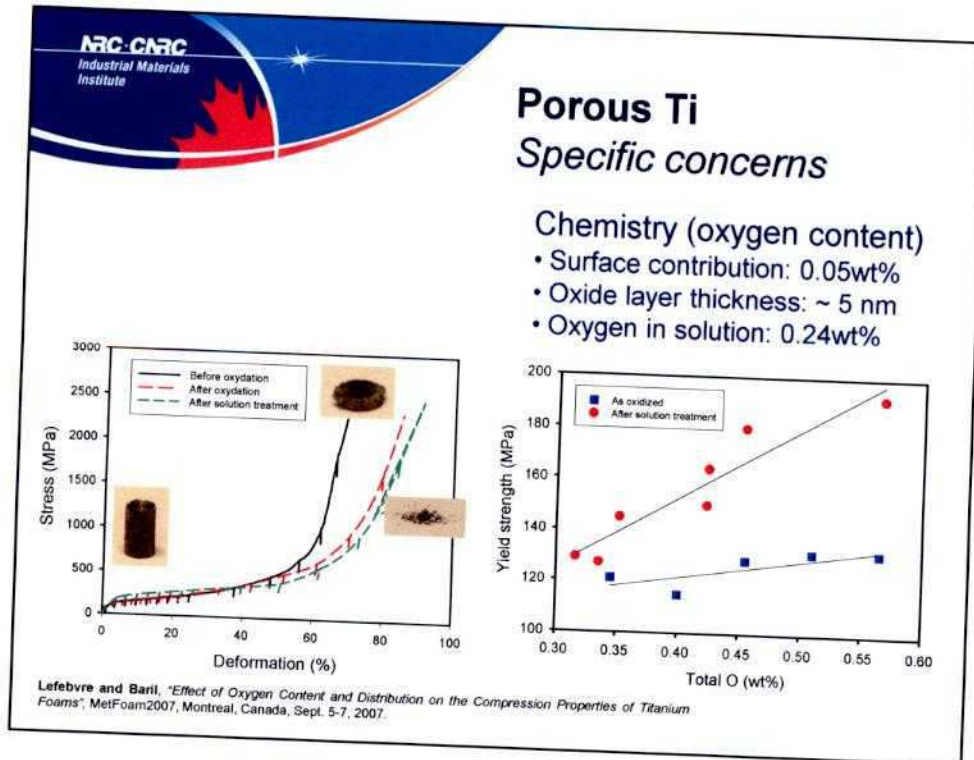
Ti-Foam characteristics

- Density: 50% open
- Surface area: 0.05 m²/g
- Total oxygen: 0.29 wt%
- Surface oxide contribution: 0.06wt%
- Oxide thickness: ~ 6 nm
- Oxygen in solution: 0.23wt%

The figure shows five cylindrical Ti-foam samples sintered at different temperatures: As sintered, 300C, 400C, 425C, and 450C. An arrow points to a single cylindrical sample labeled 'Solutionized', which has been treated for 1h at 1000°C under high vacuum.

Oxydation in 20%O₂/Argon: 1h

1h at 1000°C under high vacuum



Conclusions

The oxygen content of the final component is mainly determined by :

1. Powder oxygen content (process, size distribution, surface area)
2. Thermal processes above 400°C

When carefully selected, binder has minimal contribution to the total oxygen content.

The specification of the total oxygen content for porous titanium application should also take into account the surface area of the material.