High throughput screening of Pd-alloys for H_2 separation membranes studied by hydrogenography and CVM

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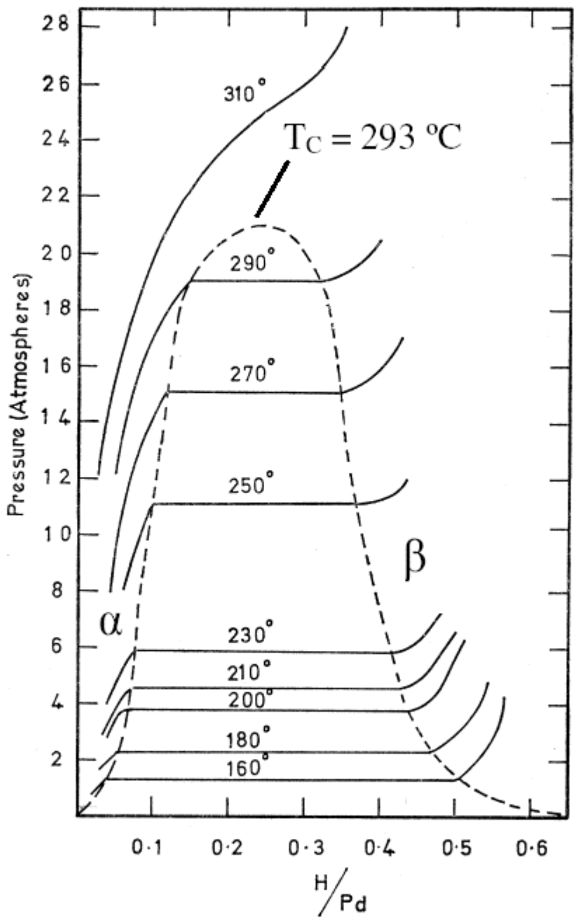
Delft University of Technology

Phase diagram Pd hydride



Plots of p-C curves after Bruning and Sieverts (1933) showing:

-The co-existence region for α and β Pd hydride

-T>300°C one Pd hydride phase

Drawbacks

-Volume expansion 10% upon hydriding

-Sensitive to poisoning

-Membrane failure above 600°C, due to grain coarsening

► Strong need for better materials: binary (ternary) alloys!!

With of course > competitive permeability

High throughput screening

Firstly what can we predict theoretically?

Secondly what would be the holy grail?

- Deposit a (part of a) phase diagram, binary or ternary
- Determine hydrogen absorption of all compositions
- Determine permeability of all compositions
- Determine cyclic behavior of all compositions
- Poison the surface and look for the differences

All in one or two experiments!

Statistical thermo: CVM

Energy functional (terms of clusters) → phase boundaries (v)

$$\Omega(\mathrm{v}, T, \mu_1^*, \mu_2^*) = E - TS + p\mathrm{v} - \sum_{n=1}^{2} \mu_n^* x_n + \lambda(1 - \sum_{ijkl} z_{ijkl}^{\alpha\beta\gamma\delta})$$

(entropy, volume)

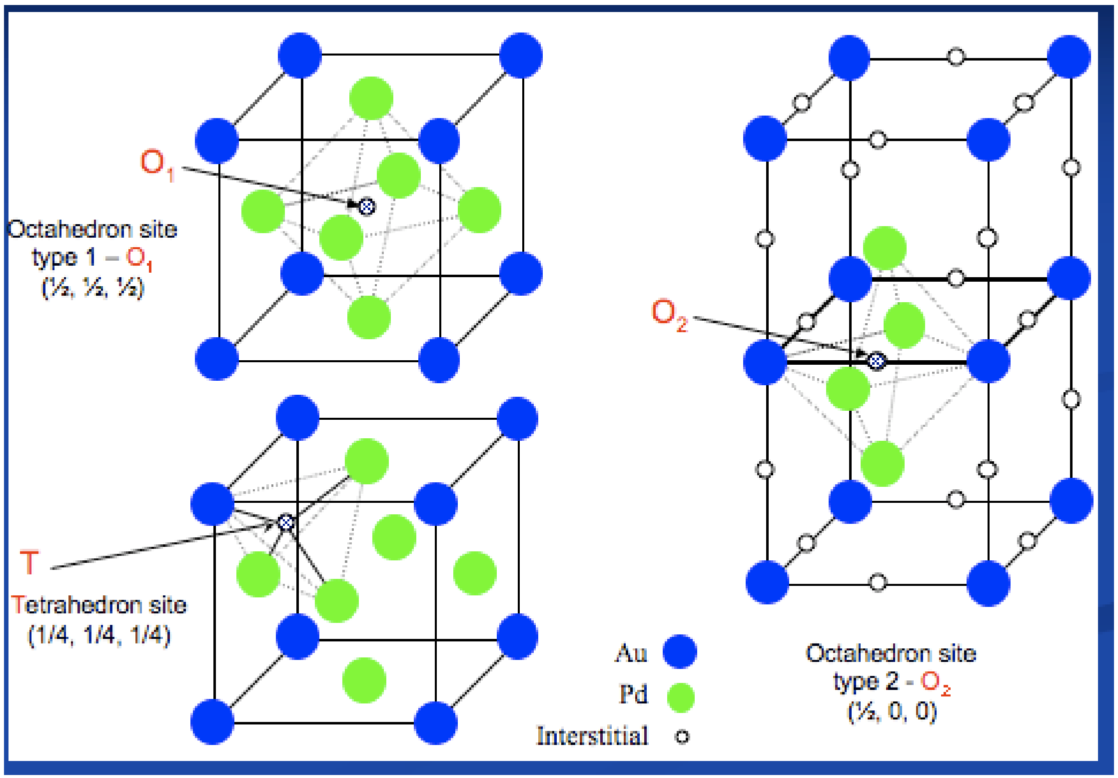
Internal energy :

- ab initio (new alloys) → effective cluster interactions
- pair interaction energies (experimental data)

TUDELFT group Böttger

Possible H positions in $L1_2$

$L1_2$ structure



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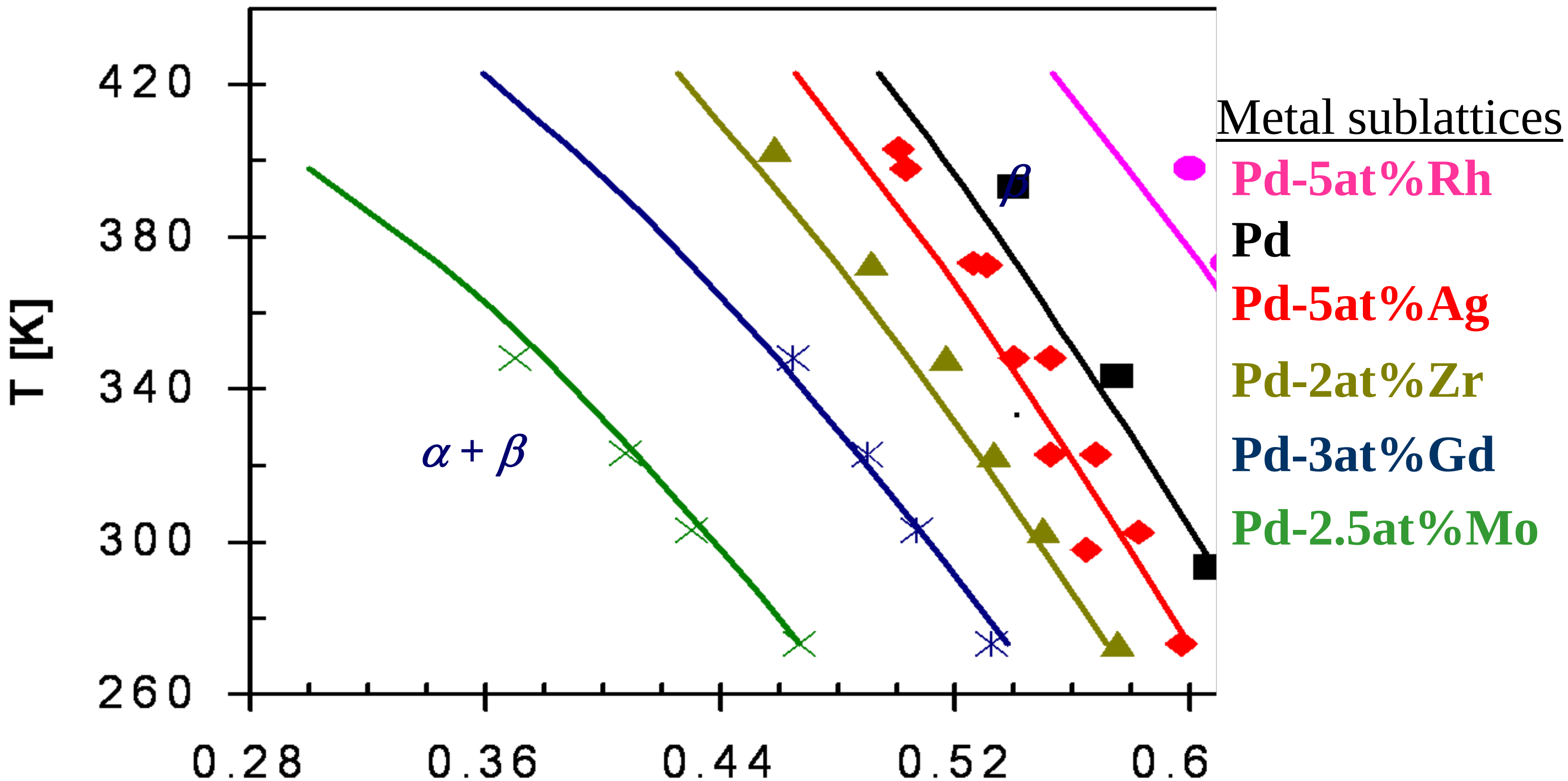
Pair interactions + CVM

Lines - CVM results

Symbols - Experimental data



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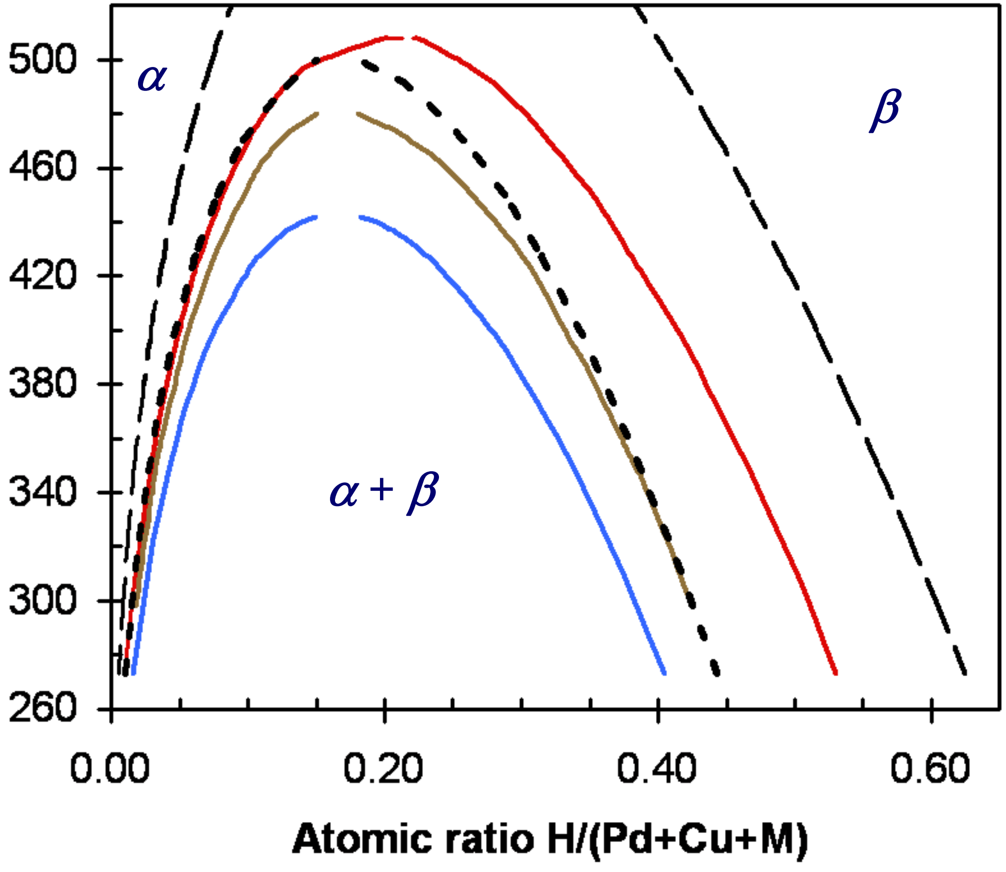
Prediction $Pd_{85}Ag_{(15-x)}M_x$-H systems

Temperature (K) *vs* composition



$Pd_{85}Ag_5Cu_{10}$

$Pd_{85}Ag_5Zr_{10}$

$Pd_{85}Ag_{10}Zr_5$

Pd - dashed line

$Pd_{90}Ag_{10}$ - dotted line

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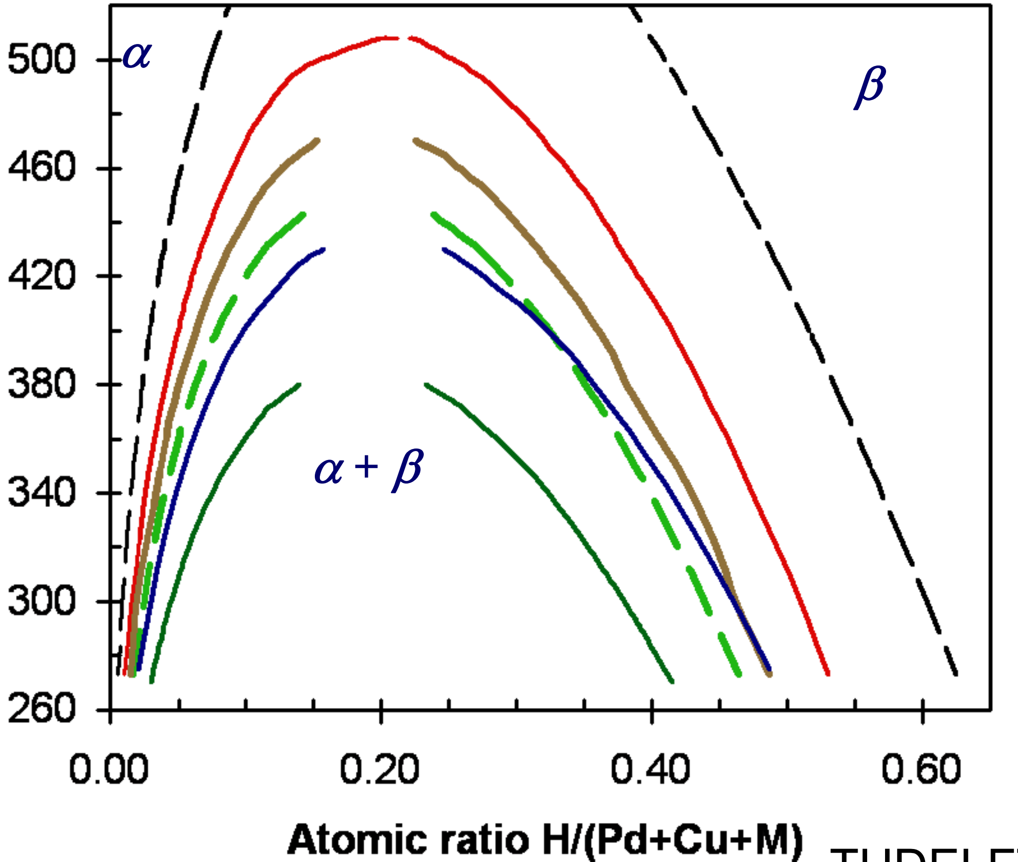
Prediction $Pd_{85}Cu_{10}M_5$-H systems

Temperature (K) *vs* composition



Pd

$Pd_{85}Cu_{15}$

$Pd_{85}Cu_{10}Ag_5$

$Pd_{85}Cu_{10}Zr_5$

$Pd_{85}Cu_{10}Gd_5$

$Pd_{85}Cu_{10}Mo_5$

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Overview results predicted systems

Alloy	T_c (K)	$\Delta V_{\beta-\alpha}/V_{\alpha}$(%)
$Pd_{85}Cu_{10}Mo_5$	385	5.8
$Pd_{85}Cu_{10}Gd_5$	475	7.2
$Pd_{85}Cu_{10}Zr_5$	471	7.9
$Pd_{85}Cu_{10}Ag_5$	508	9.1
$Pd_{85}Ag_5Zr_{10}$	442	6.6
$Pd_{85}Ag_{10}Zr_5$	480	7.6

Pd: T_c = 560 K, $\Delta V_{\beta-\alpha}/V_{\alpha}$ =10.7 %

No information on permeability, however, from CVM

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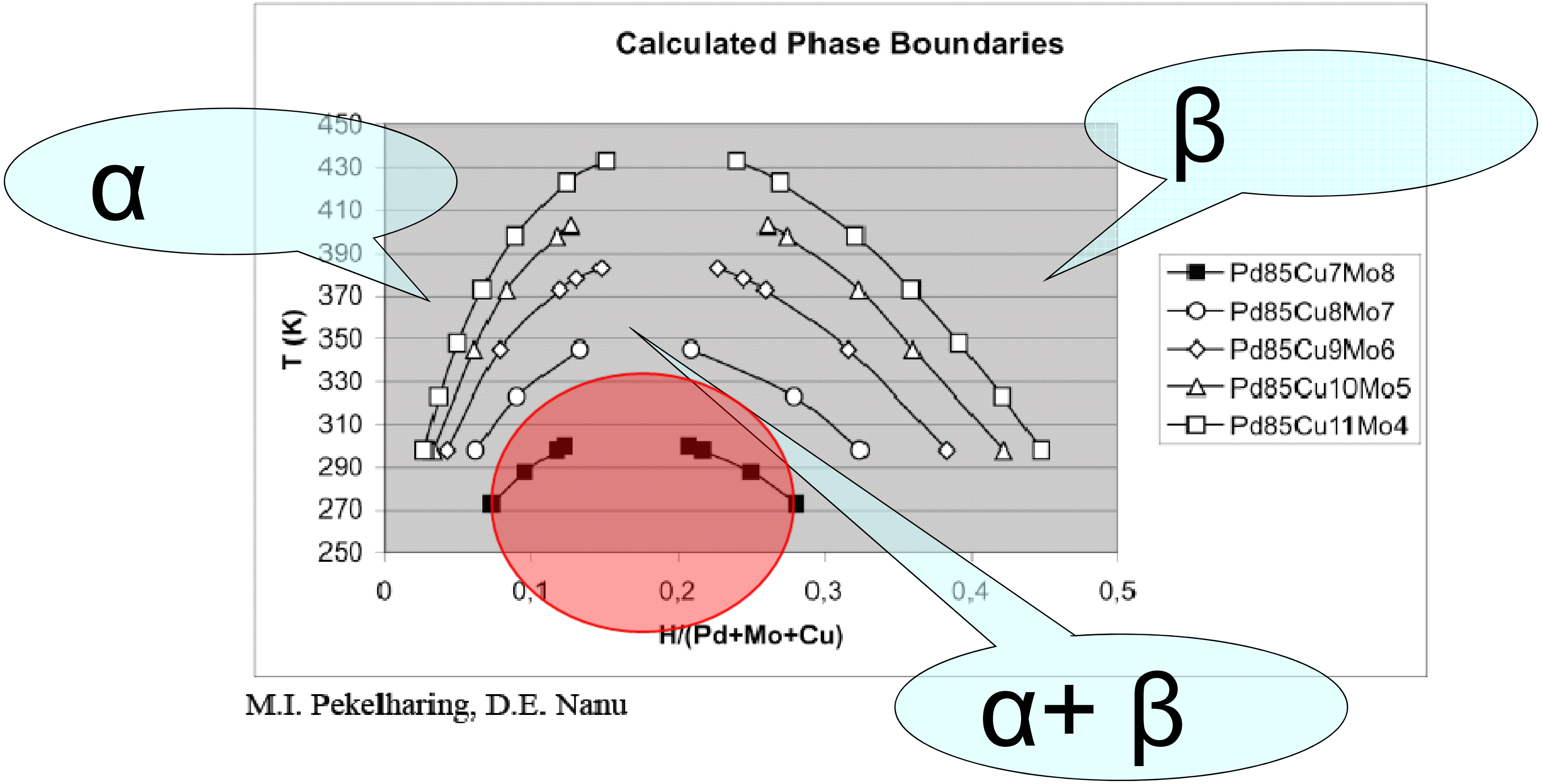
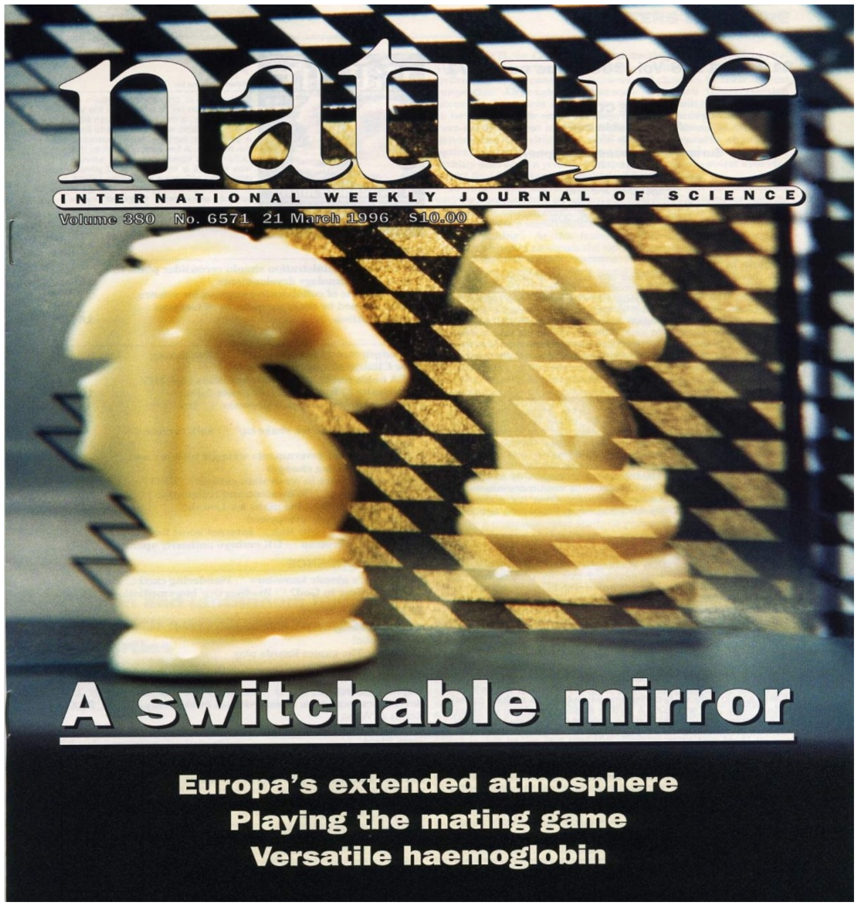
CVM: T_c for Pd-Cu-Mo alloys

Results CVM calculations $PdMo_xCu_{(1-x)}$



M.I. Pekelharing, D.E. Nanu

High throughput screening of H_2 membrane alloys: basics

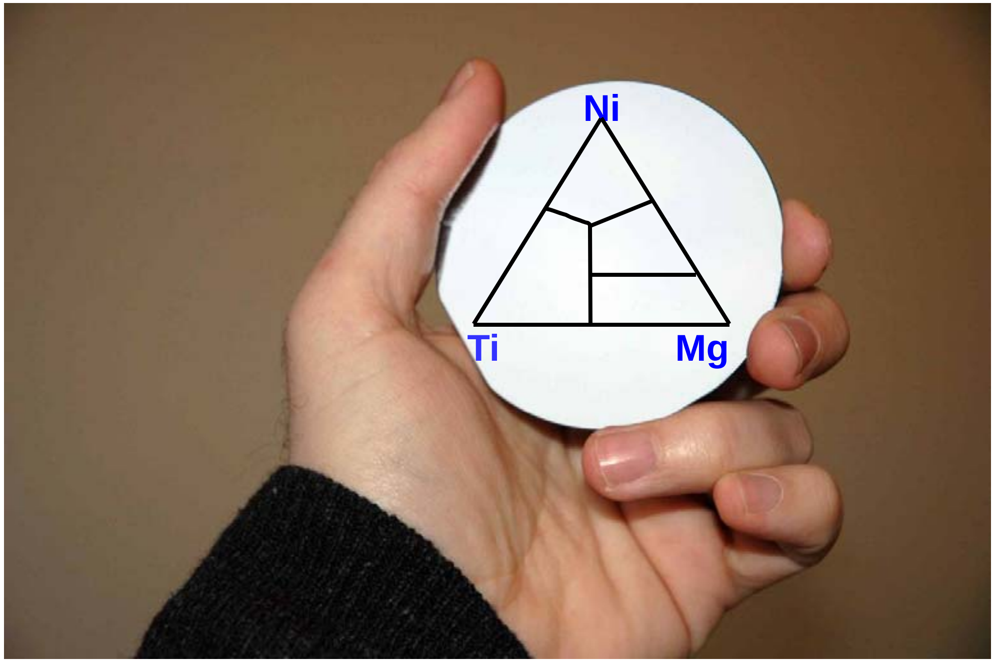


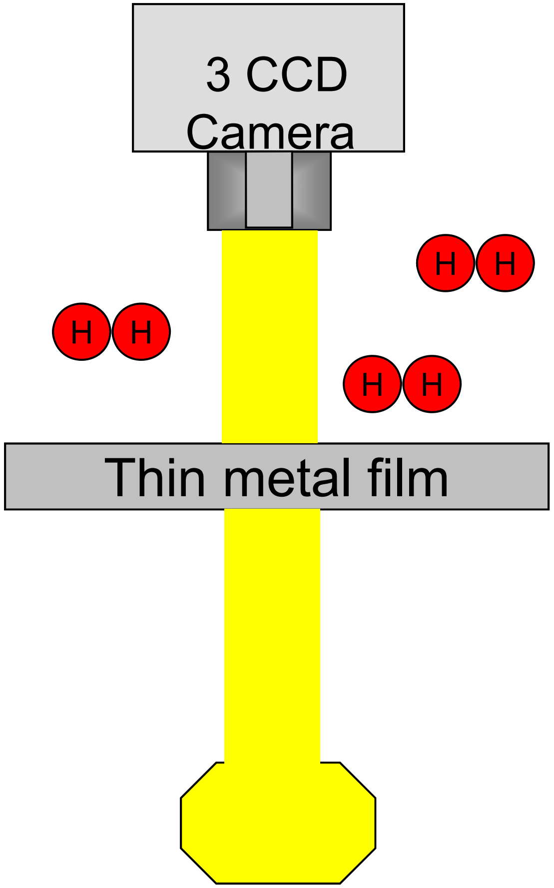
Y: Metal

YH_2 : Metal

YH_3 : Insulator

High throughput screening: hydrogenography

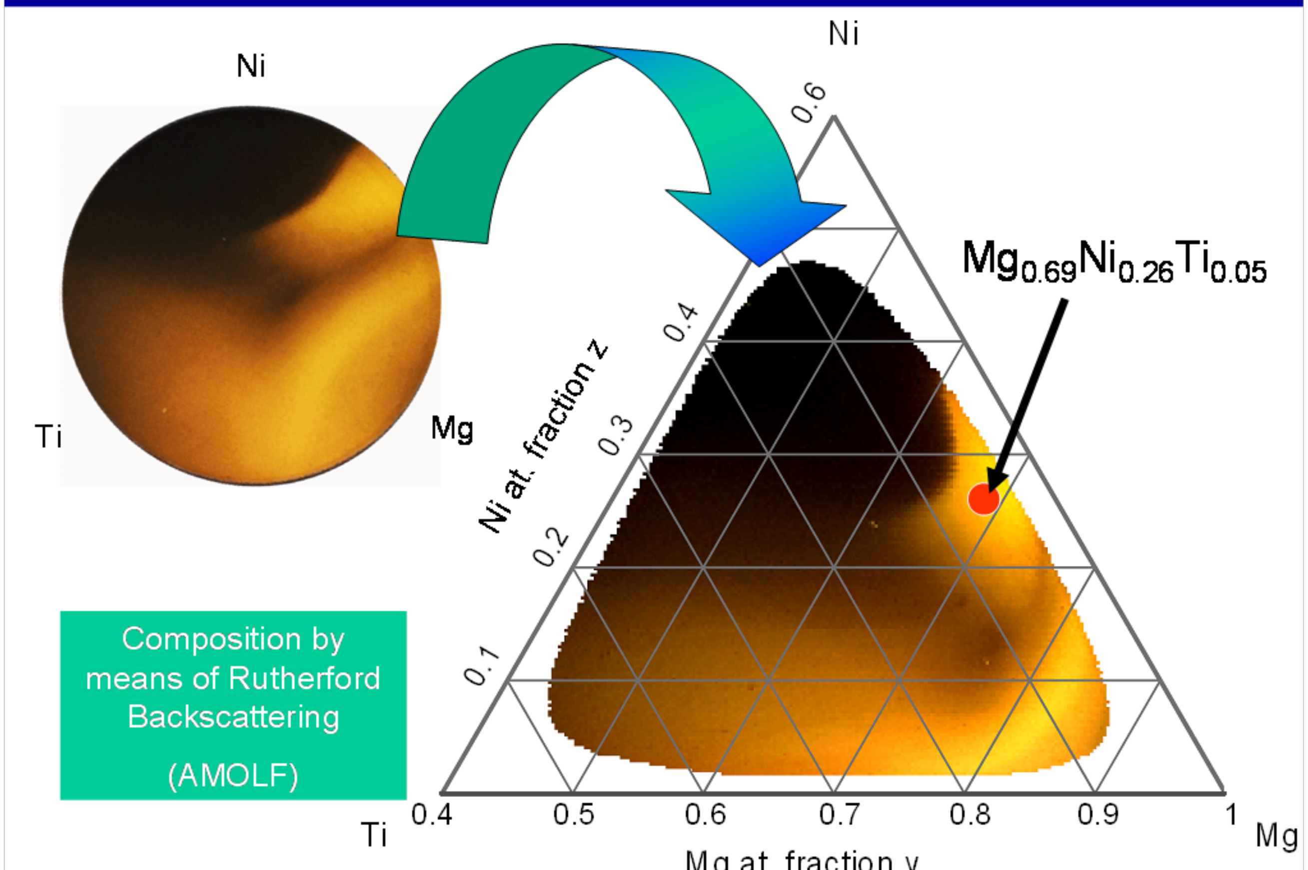




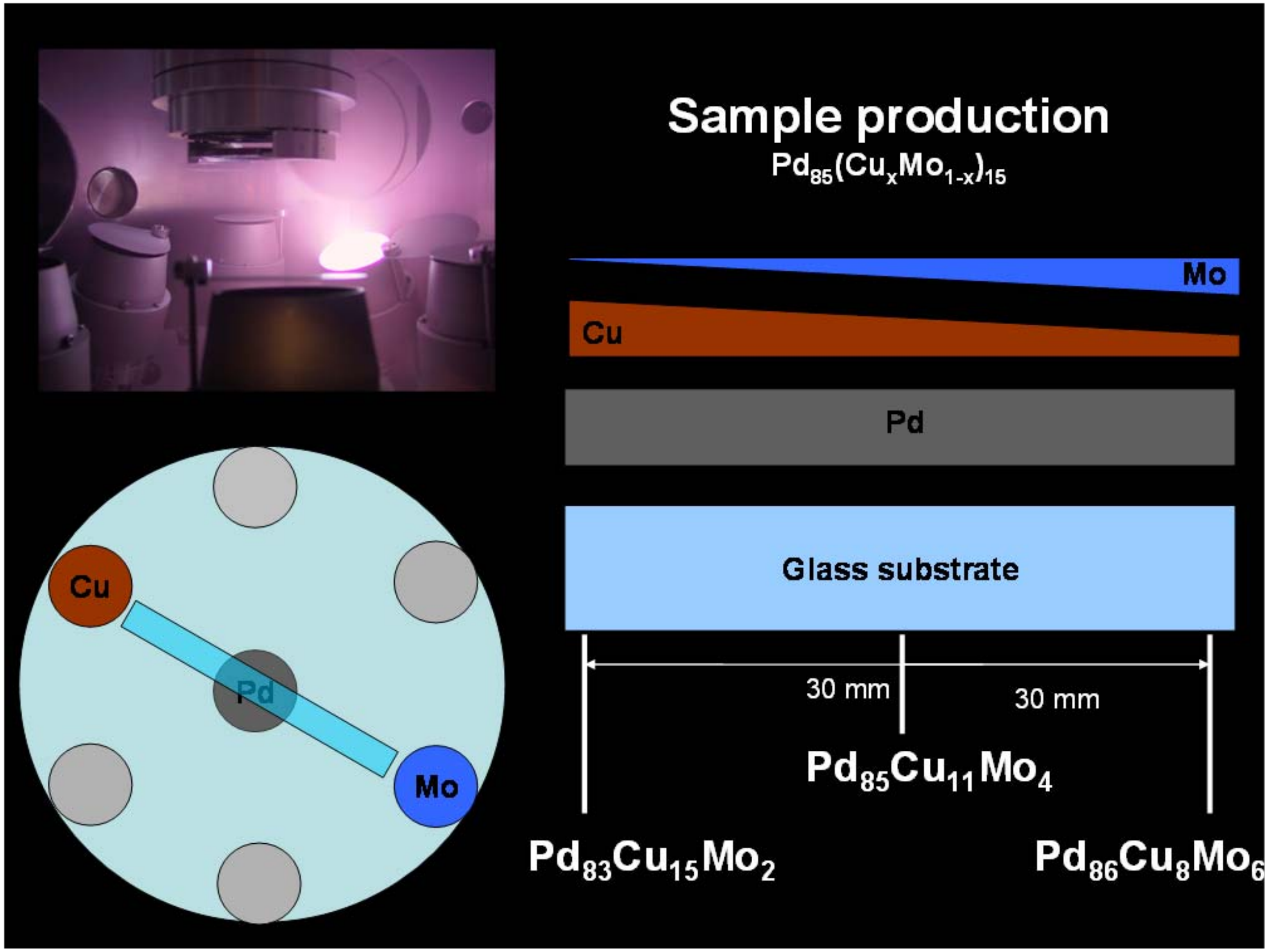
Source: Adv. Mater. 2007, 19, 2813-2817
Scripta Materialia 56 (2007) 853-858

Optical response

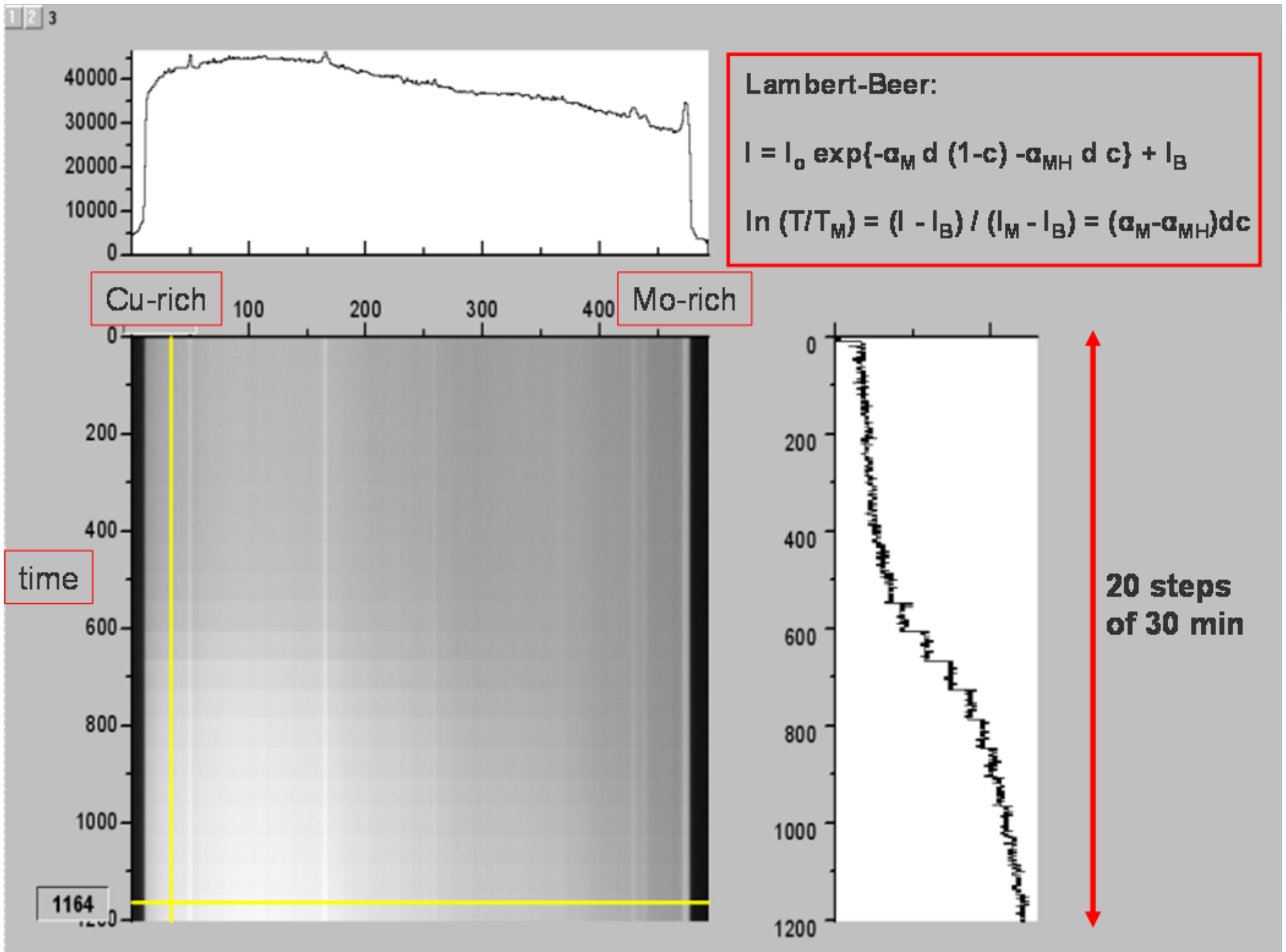
Optical transmission in ternary diagram



Hydrogenography for Pd alloy research



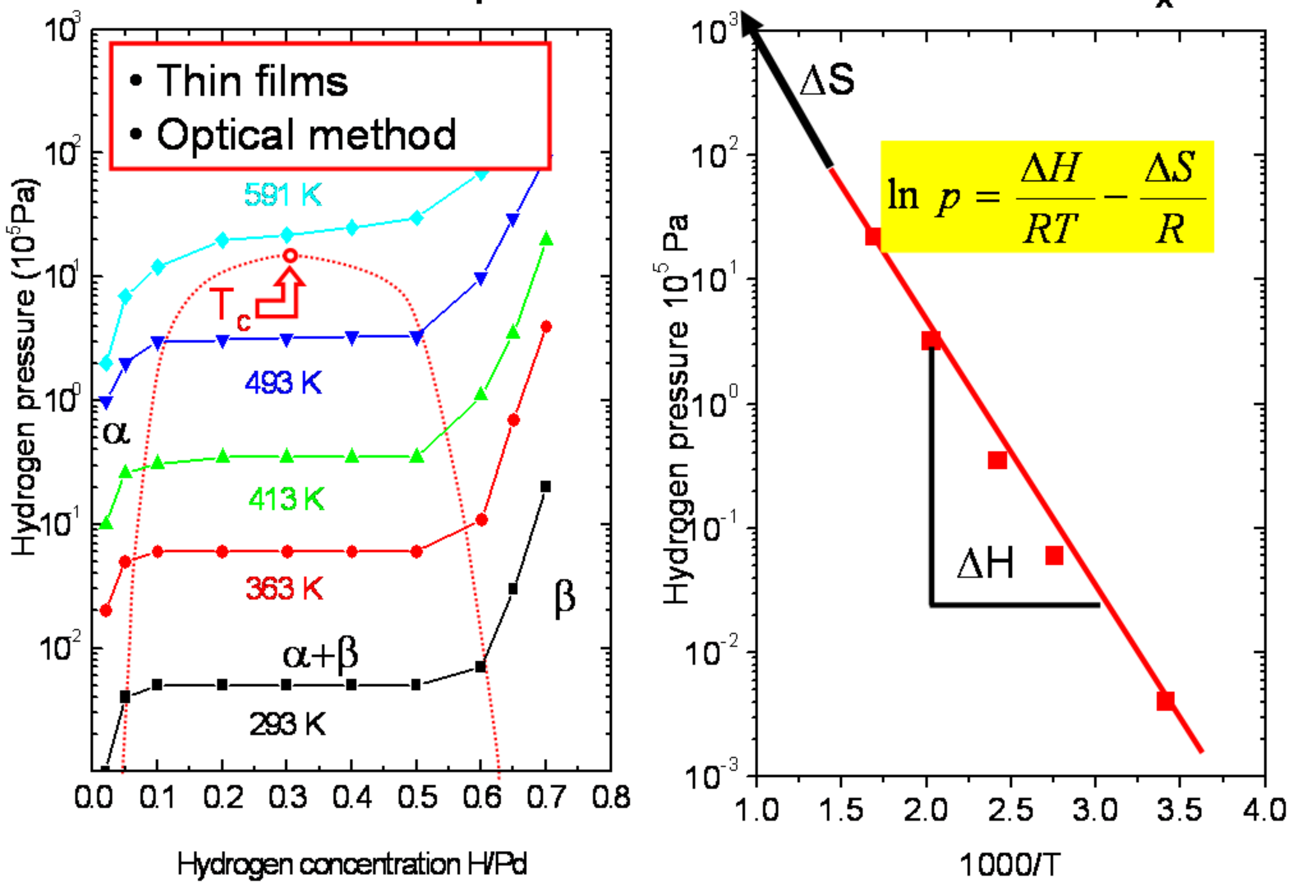
Hydrogenography for Pd alloy research



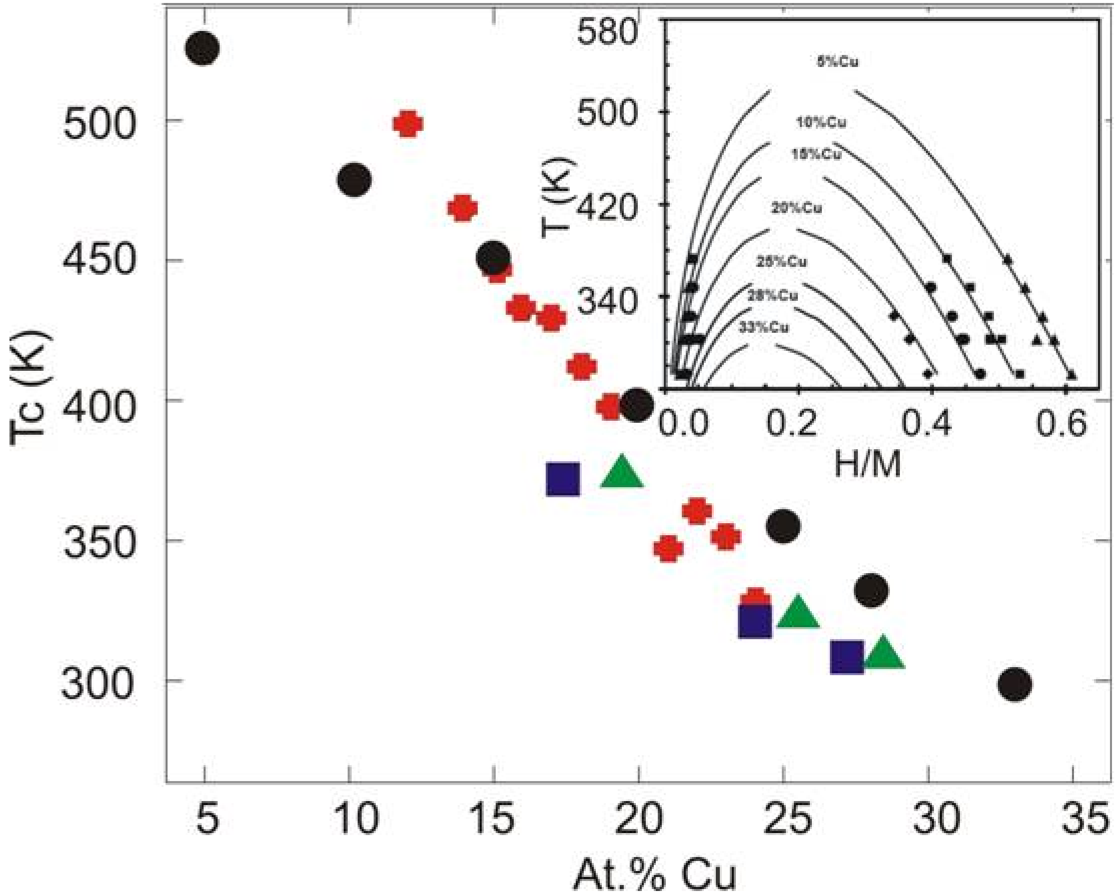
Results

R. Gremaud

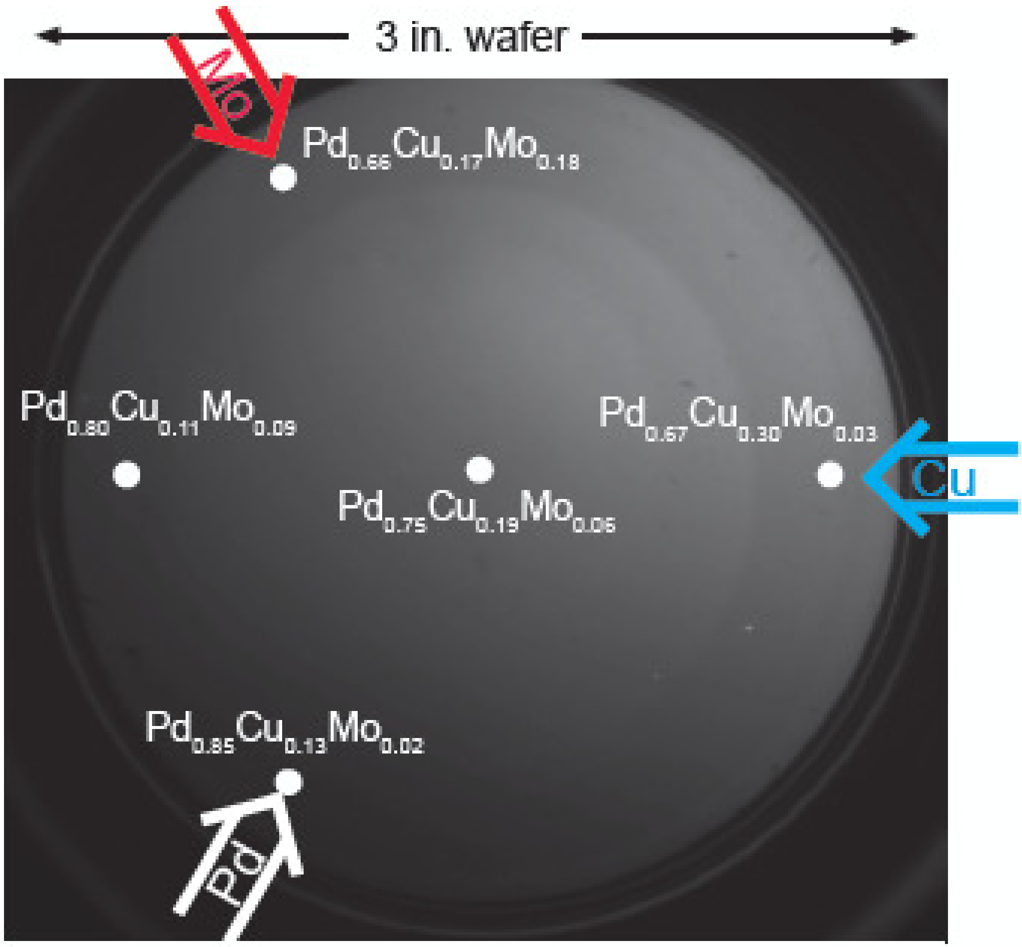
Pressure-composition isotherms of PdH_x



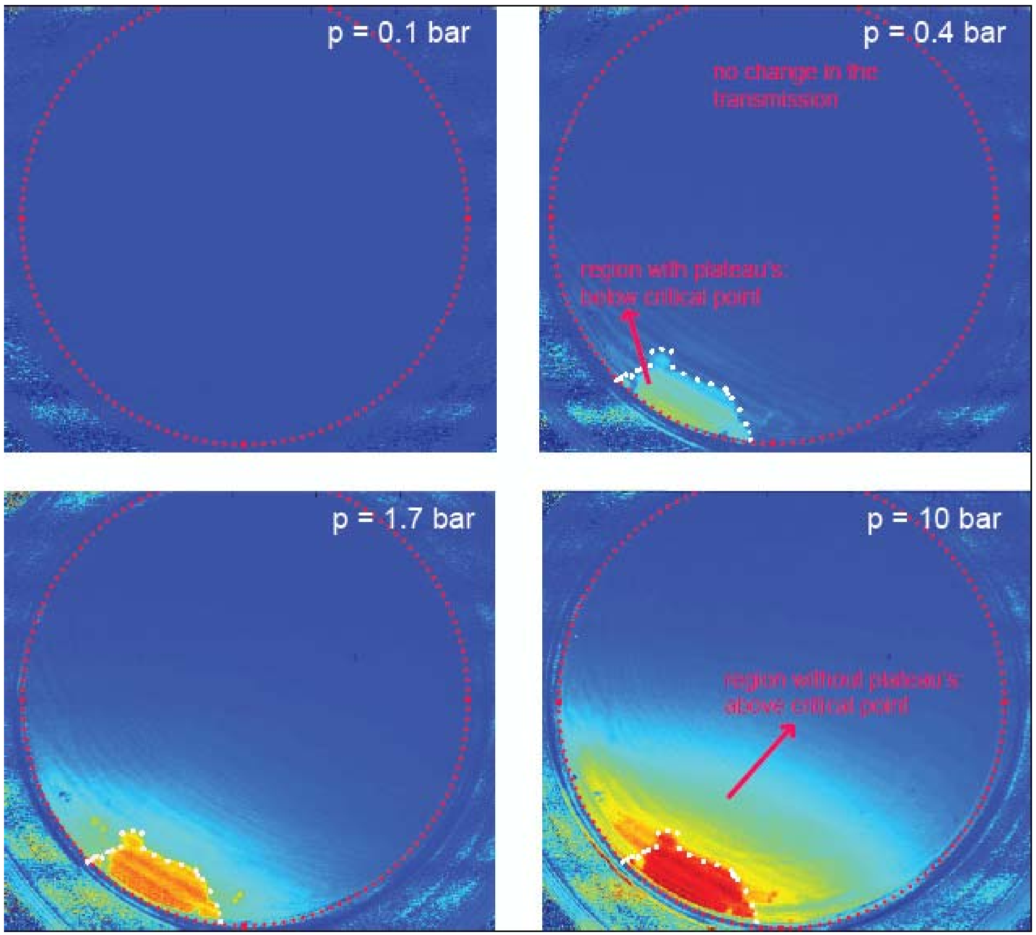
Pd-Cu: CVM (•) meets hydrogenography (▲) and bulk



Compositional lay-out: Mo

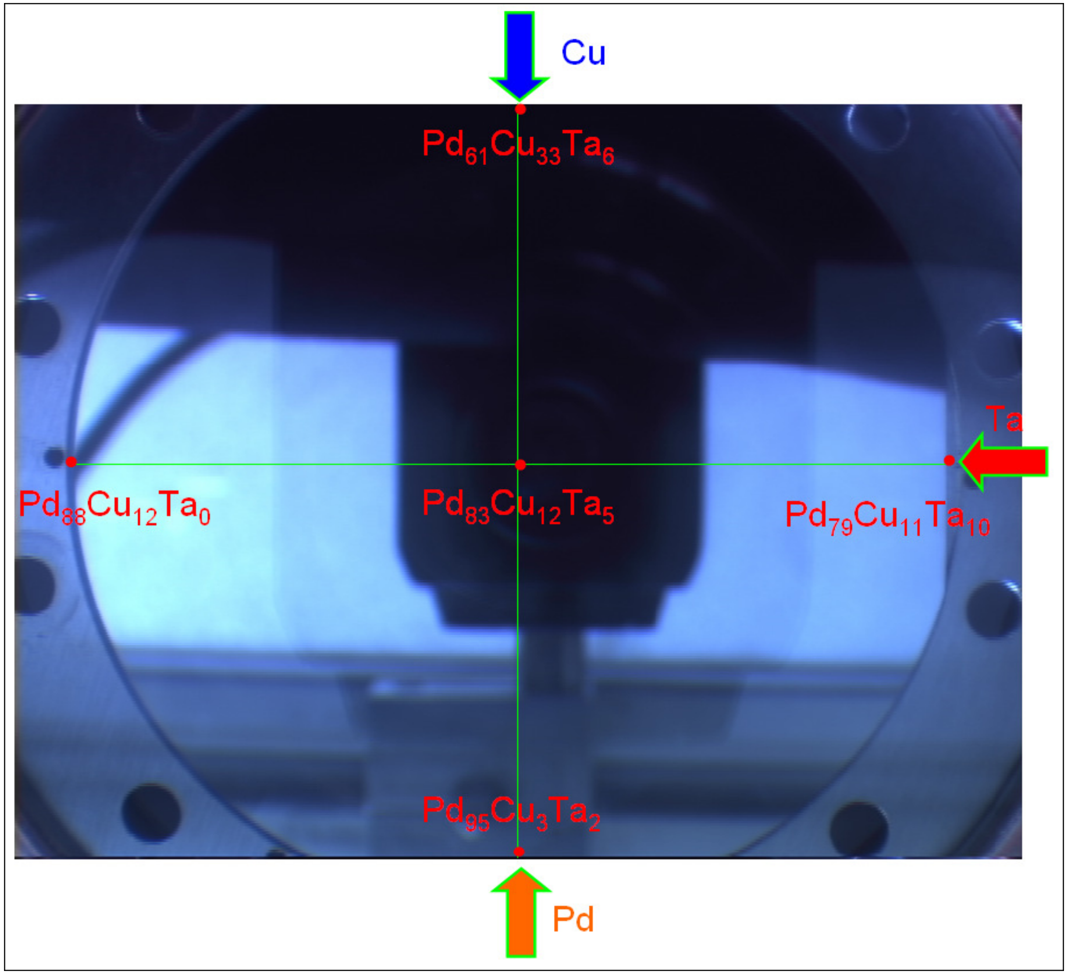


Pd-Cu-Mo

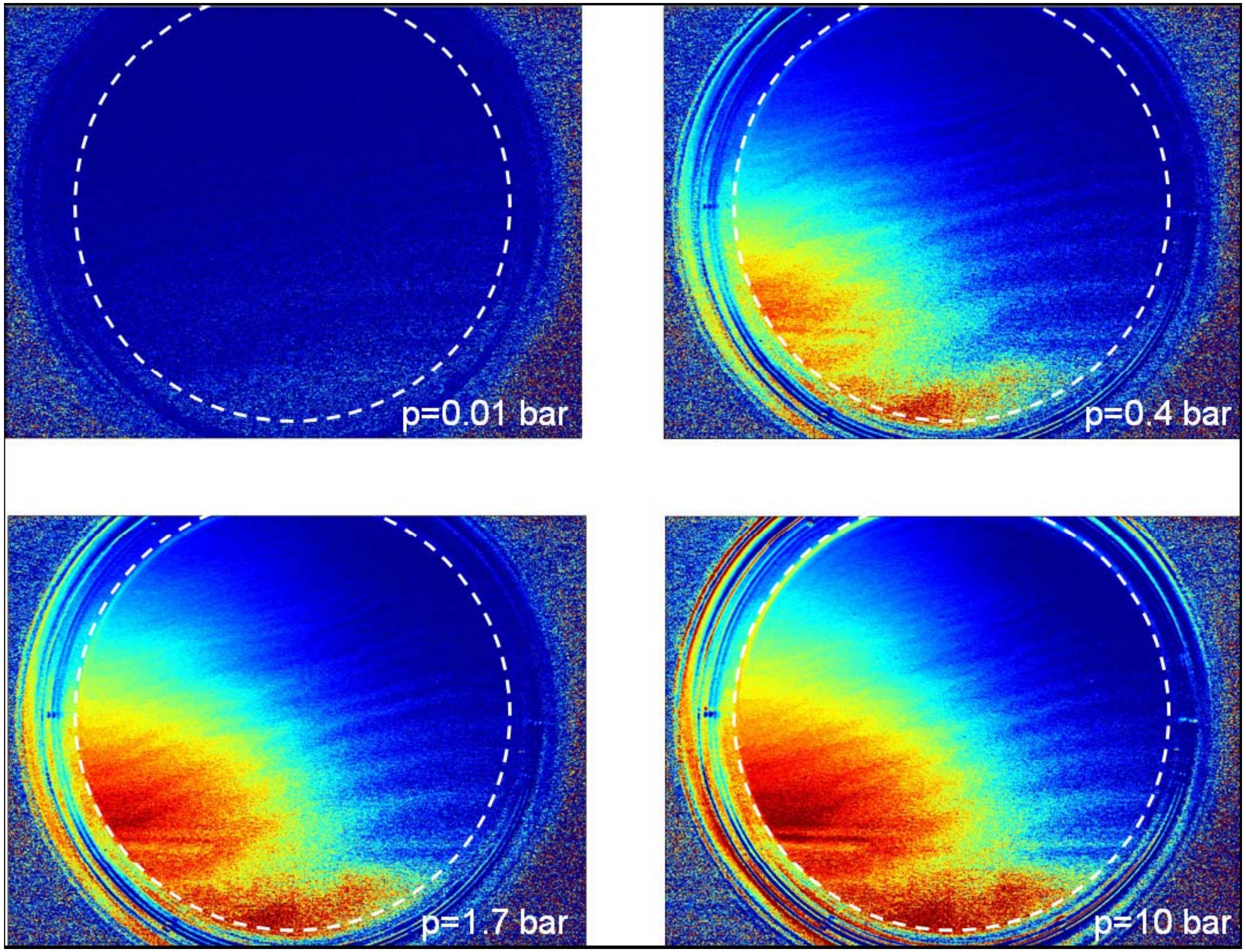


p = 0.1 bar
p = 0.4 bar
no change in the transmission
region with plateau's: below critical point
p = 1.7 bar
p = 10 bar
region without plateau's: above critical point

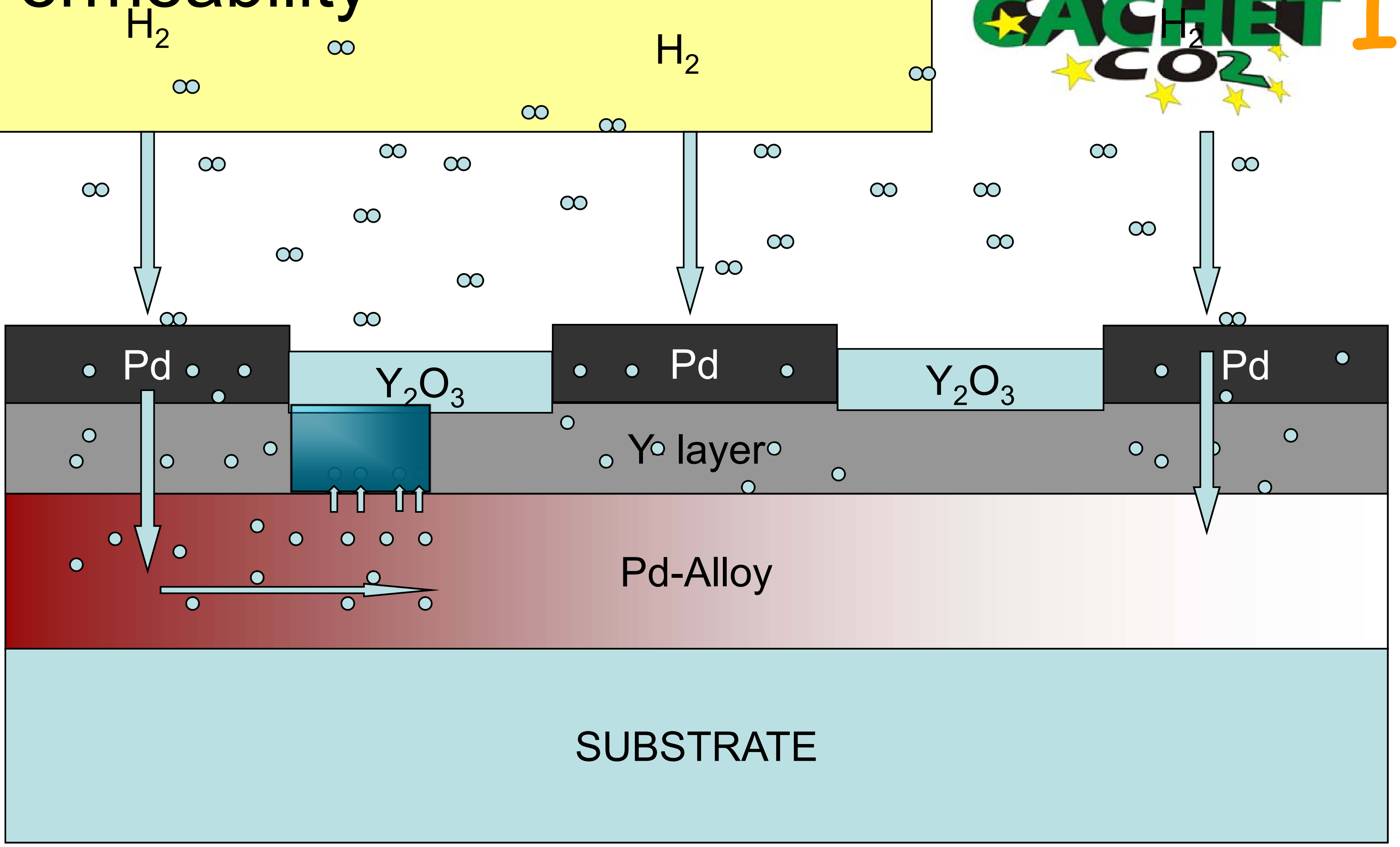
Compositional lay-out: Ta



Pd-Cu-Ta

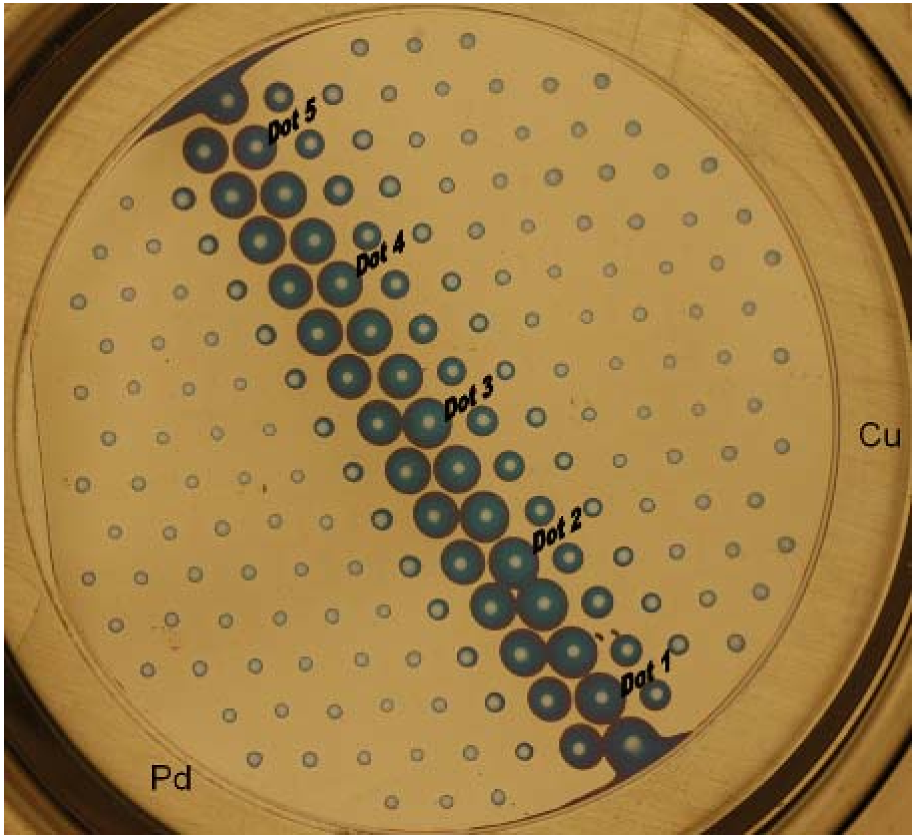


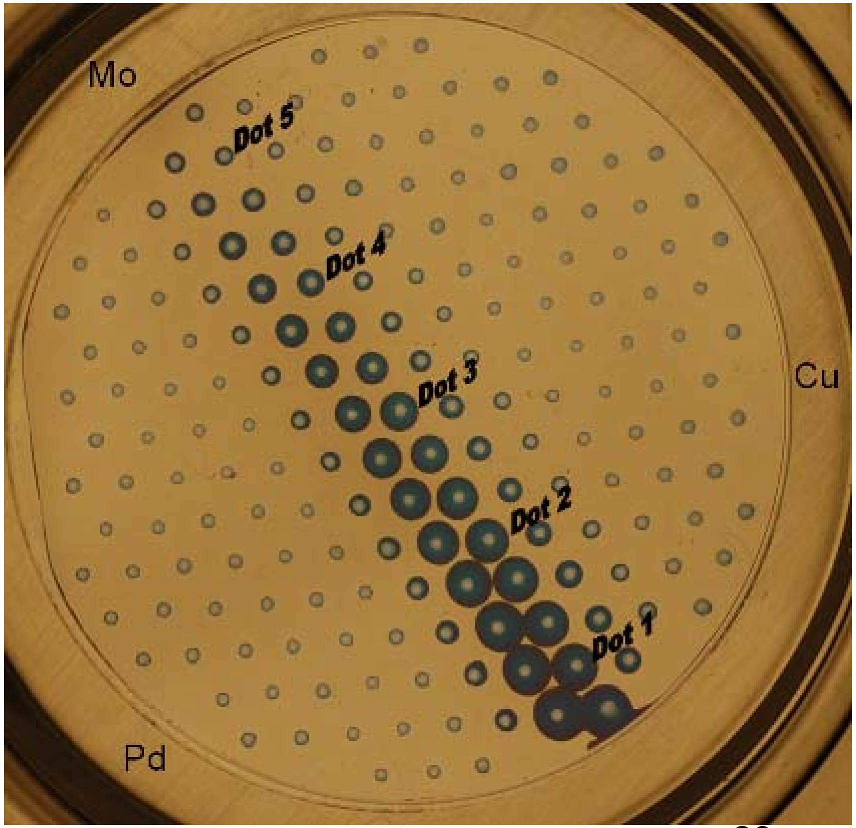
Permeability



Since lateral diffusion in Y is much smaller than in the alloy, the image of the loading of the alloy is reflected by the coloration of the Y layer being loaded via the alloy layer: this is a measure for the intrinsic permeability of the alloy.

Permeation dots for Pd-Cu &Pd-Cu-Mo





Final remark

This high throughput technique in combination with CVM is the way to go!!

CVM-Hydrogenography & Permeability Team

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