4TU.HTM & M2i Joint Workshop 22-10-2020

Modelling of surface segregation for Pd-alloys in vacuum and gas environments

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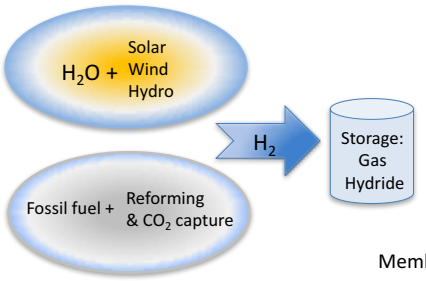
H_2 Production and Gas Separation



95% H_2 from fossil fuel

Hysep-module, Chieti test plant, Italy
Hysep.com

Membrane reactor for H_2 production:

Steam reforming: $CH_4 + H_2O \rightleftharpoons 3\ H_2 + CO$ ($\Delta H = 206$ kJ/mol)

Water-gas shift: $CO + H_2O \rightleftharpoons H_2 + CO_2$ ($\Delta H = -41$ kJ/mol)

$CH_4 + 2\ H_2O \rightleftharpoons 4\ H_2 + CO_2$

remove H_2 from reaction mixture

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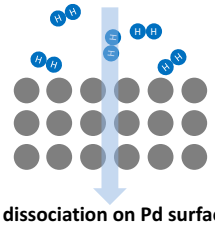
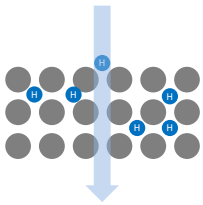
Pd-based Membranes

- Operating conditions: 550-950 K, 10-50 bar
- Impurities: H_2O, H_2S, CO, CO_2

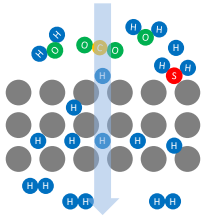
- High selectivity
- High permeability



H_2 dissociation on Pd surface



Interstitial diffusion



Separation from gas mixtures

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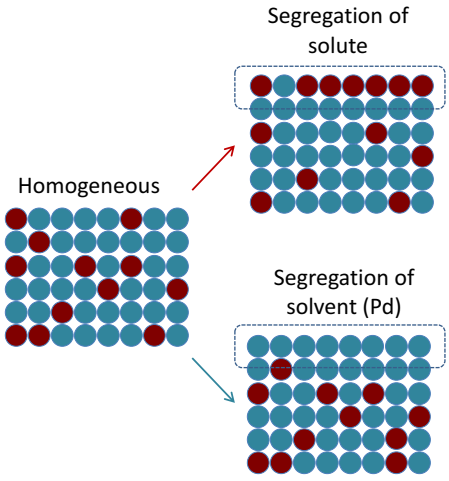
Surface Segregation

Pd – Alloys in Vacuum/ H_2 gas

Binary Alloy	Segregating Element Vacuum / H_2
Pd-Ag	Ag / Pd
Pd-Au	Au / Pd
Pd-Cu	Cu / Pd
Pd-Ni	Pd / Ni
Pd-Pt	Pd / Pd
Pd-Hf	Pd / Pd
Pd-Fe	Pd / Fe



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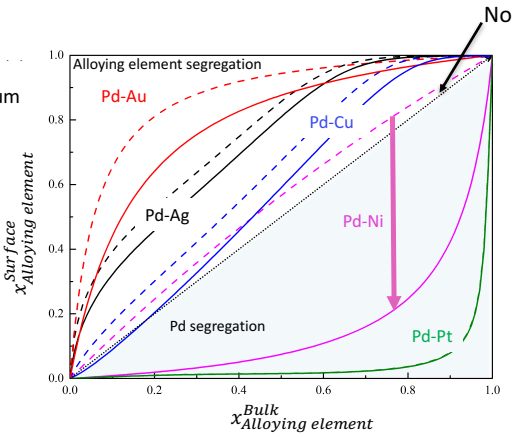
Binary Alloys : Calculations Result

Pd-A in Vacuum

T=600 K



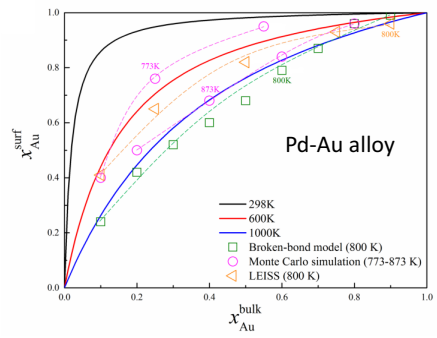
Solid lines:
(111) plane
with elastic energy

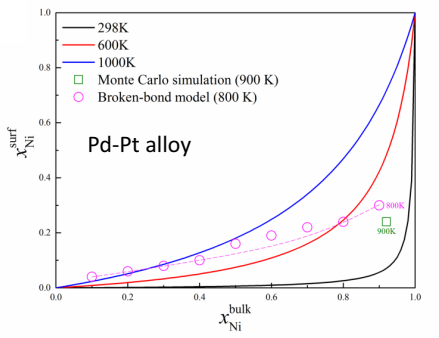
Dashed lines:
(111) plane
without elastic energy

Elastic strain energy can be the dominating factor for some alloys.

Meng, Sloof, Bottger, Int.J. Hydr. 43 (2018)2212

Calculations vs. Literature Data : Vacuum



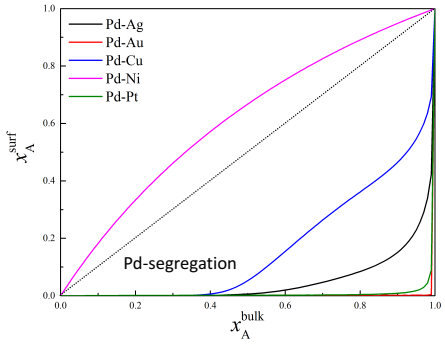


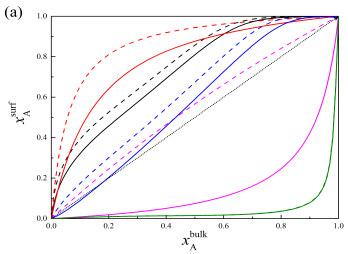
Meng, Sloof, Bottger, Int.J. Hydr. 43 (2018)2212

Surface Segregation in

T=600 K

Hydrogen adsorption and absorption

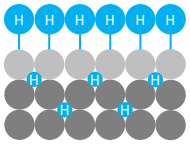




(111) Plane

Single layer adsorption

$x_H / x_M = 0.5 \quad \theta = 1$



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Ternary Alloys : Comparison with Literature

Alloy	Temperature	Literature method	Segregation elements	
			Literature	Calculation (in this work)
Fe72-Cr20-Ni8	723 K	Atom probe	Cr and Ni	Cr and Ni
Cu92-Ag1-Au7	773 K	AES	Ag and Au	Ag and Au
Ni50-Al40-Cu10	1000 K	Monte Carlo	Al	Al
Pt83-Pd15-Rh2	1200 K	Monte Carlo	Pd	Pd

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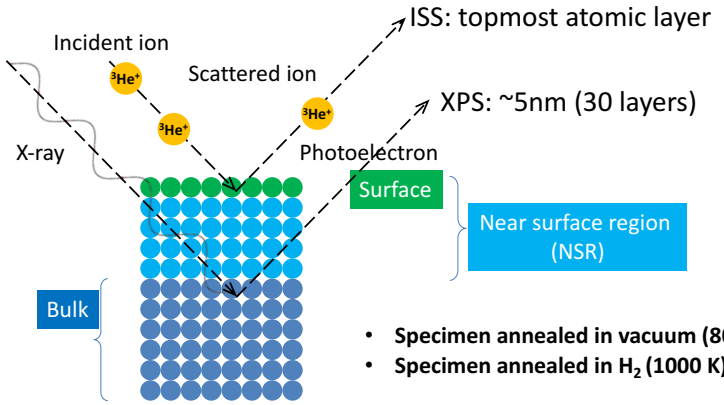
Meng, Brouwer, Sloof, Böttger, *Adv. Mater. Interfaces* **2020**, *7*, 1901784

Experimental Analysis: XPS & LEISS



- **Specimen annealed in vacuum (800/1000 K)**
- **Specimen annealed in H_2 (1000 K)**

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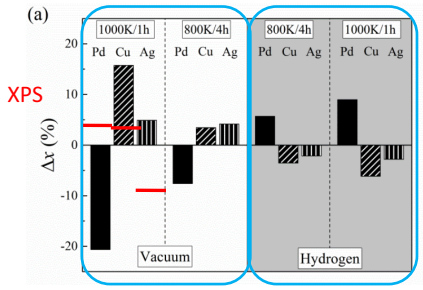
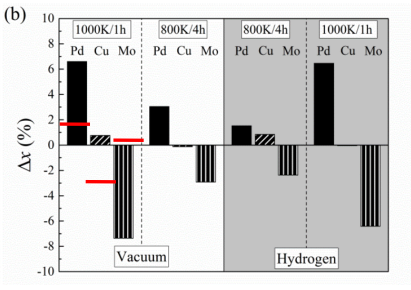
Ternary Alloys Segregation : LEISS results

Pd60Cu30Ag10



Segregation of Cu and Ag in vacuum
Segregation of Pd in H_2

Pd85Cu5Mo10



Segregation of Cu and Pd in vacuum
Segregation of Pd in H_2

XPS (near surface region) and LEISS (top layer) show different trends

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Experimental Results: LEISS

Alloy	Condition	Calculation (at.%)			Experiment result (at.%)		
		Cu	Ag	Mo	Cu	Ag	Mo
Pd-Cu-Ag	Before segregation	30.0	10.0		28.6	8.3	
	1000 K in vacuum	54.4	16.5		45.4	15.3	
	1000 K in H_2	29.9	3.9		23.2	7.6	
Pd-Cu-Mo	Before segregation	5.0		10.0	5.2		10.9
	1000 K in vacuum	0		0	6.0		3.6
	1000 K in H_2	0		0	5.2		4.5

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Meng, Brouwer, Sloof, Böttger, *Adv. Mater. Interfaces* **2020**, *7*, 1901784

Conclusions

- Segregation in binary alloys:
  - Predictive model (vacuum or gas environment)
  - Dominated by surface energy
  - Composition change in near surface region
- Segregation ternary alloys:
  - Qualitative model (vacuum or gas environment)
  - Competition between surface energy and mutual atom interactions
  - Composition change in near surface region (differences XPS, LEISS)

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Surface and Interface Engineering

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13