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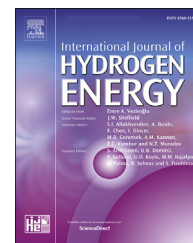
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Surface segregation of Pd–Cu alloy in various gas atmospheres



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HIGHLIGHTS

- Surface segregation of Pd–Cu was studied in vacuum and various gas atmospheres.
- Cu content of the surface region was measured by LEISS and XPS respectively.
- Opposite surface segregation behaviours were observed in vacuum and in H₂ or CO.
- Effect of gas adsorption on surface segregation were theoretically discussed.

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ABSTRACT

Pd–Cu alloys have been investigated as promising candidates for hydrogen separation membranes. Surface segregation influences the long-term performance of these membranes since their catalytic effect is mainly controlled by the surface composition. In the present research, surface segregation of Pd-40 at.% Cu alloy in vacuum and various gas atmospheres (H₂, CO and CO₂) was investigated with both XPS and LEISS probing different depths below the surface. Adsorption of H₂ and CO on the surface has a significant impact and the surface segregation trend can be reversed as compared to segregation in vacuum, however, CO₂ has almost no influence on the segregation behaviour. A thermodynamic model is also presented to explain these phenomena and to understand surface segregation behaviour of binary alloys in various gas atmospheres. The results can be considered as basic guidelines to design novel alloys for hydrogen separation membranes and predict their long-term performance under actual working conditions.

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Introduction

The application of Palladium-based alloy membranes is the most promising and practical method for hydrogen separation for hydrocarbon reforming [1]. Pd binary alloys may possess outstanding properties that overcome disadvantages of pure Pd, for example hydrogen embrittlement [2–5]. Some Pd alloys

have been developed and proven to be more permeable for hydrogen than pure Pd. Among them, Pd–Cu alloys that also show better resistance to sulphur impurities, which benefits the long-term stability of membrane reactors [6]. Considering the FCC–BCC phase transformation, Pd-40 at.% Cu alloy exhibits structural stability within the operating temperature range [7]. The hydrogen permeability of a Pd-40 at.% Cu alloy covered V–15Ni composite membrane has also been studied

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showing satisfying results [8,9]. However, surface segregation is a crucial problem restricting further application of Pd-based alloy membranes, as the hydrogen dissociation is mainly determined by the surface composition, especially the outermost atomic layer [10,11]. Hence, a quantitative investigation of the surface segregation is paramount to improve the performance of Pd–Cu alloy membranes for hydrogen separation. From both theoretical and experimental studies, it has been reported that Cu segregates to the surface of Pd–Cu alloy in vacuum [12,13]. However, the actual working atmosphere is much more complex as it includes H_2 and minor impurity gases [14]. There are still some ambiguities about the effect of the various gas atmospheres on the surface segregation, such as H_2 , CO, CO_2 as well as their mixtures.

In the present research, surface segregation of Pd-40 at.% Cu alloy was investigated in vacuum and various gas atmospheres with both X-ray photoelectron spectroscopy (XPS) and low energy ion scattering spectroscopy (LEISS) probing different depths below the surface. A thermodynamic model is presented based on the atom exchange approach to understand the segregation behaviour. The effect of adsorption of gases on the surface segregation is quantitatively evaluated and discussed.

Experiments

A foil sample of Pd-40 at.% Cu alloy with a thickness of 100 μm (Goodfellow, Huntingdon, UK) was used for the analysis of surface segregation. The surface was first fine polished with an oxide polishing suspension with a particle size of 0.05 μm . Then repeated Ar^+ ion sputtering and subsequent recovery by short time heat treatment at 800 K for 10 min in UHV chamber (base pressure $<10^{-7}$ Pa) were executed to obtain a clean surface without C and O, as well as making sure that the elemental composition in the near surface region is close to that of the bulk. Both X-ray photoelectron spectroscopy and low energy ion scattering spectroscopy (XPS and LEISS, PerkinElmer PHI 5400, Eden Prairie, USA) were applied at room temperature to determine the elemental composition of the surface. The XPS spectra were obtained using a non-monochromatic Al K α radiation generated with an Al anode X-ray source operated at 200 W and 13.1 kV. The main photoelectron lines of each element (Pd 3d $_{5/2}$ 335.0 eV, Pd 3d $_{3/2}$ 340.3 eV, Cu 2p $_{3/2}$ 933.0 eV) were recorded with a step size of 0.5 eV and a dwell time of 1.25 s using a spherical capacitor analyzer set with a pass energy of 71.55 eV. The photoelectrons were collected at take-off angles of 45° and 15° with respect to the sample surface to probe different depths below the surface, corresponding with about 10 and 3 atomic layers (ALs), respectively, considering an inelastic mean free path of about 10–15 Å. The LEISS spectra with a step size of 1 eV and a dwell time of 60 s were taken with 1 keV 3He $^+$ incidence with a low current of 500 nA to minimize any effect from the ion bombardment.

After the initial surface composition was achieved, the sample was transferred from the UHV chamber to a horizontal annealing furnace (Carbolite, MTF 12/38/850, Hope, UK) equipped with a quartz tube with inner diameter of 30 mm. To this end a vacuum transfer vessel was used sealing the sample

from the atmosphere to avoid any contamination of the sample surface. Surface segregation was evoked by annealing at 1000 K for 60 min in vacuum (base pressure $<10^{-7}$ Pa), and respectively in 0.5 bar H_2 , 0.5 bar CO and 0.5 bar CO_2 , each mixed with 0.5 bar Ar for protection. In order to investigate the effect of gas mixtures, surface segregation in 0.25 bar H_2 +0.25 bar CO+0.5 bar Ar was also measured. After annealing at the target temperature, the furnace was moved away from the quartz tube to rapidly cool down the sample. Next, the sample was transferred back to the UHV chamber in the transfer vessel under the same atmosphere as used during the annealing. It was measured that the sample is cooled down to below 800 K within 30 s and to about room temperature within 5 min. Then, XPS and LEISS measurements were performed again to obtain the elemental composition upon segregation. Comparing the surface composition before and after annealing, surface segregation in vacuum and in various gas atmospheres were obtained quantitatively. Additionally, annealing at 800 K for 1 h in vacuum was applied to determine whether the elemental composition is changed during the cooling process.

Result and discussion

XPS and LEISS spectra are shown in Figs. 1 and 2, respectively. With a normalized Pd peak, the variation of the Cu peak area qualitatively represents the change of Cu content in the corresponding analysis depth below the surface. For a quantitative analysis, the composition of each element in both the first 10ALs and 3 ALs regions were calculated from the corresponding XPS peak area after Shirley background subtraction and adopting the corresponding sensitivity factors [15]. The elemental composition in the outermost AL was determined from the area of a Gaussian-fit to the LEISS peaks. All the Cu content results of different depths under the surface are listed in Table 1. As a comparison, even after annealing at 800 K for 1 h in vacuum, the Cu content at the surface is rather homogeneous (40.9 at.% for first 10 ALs, 37.7 at.% for first 3 ALs, 39.2 at.% for the outermost AL). This indicates that virtually no segregation occurs during the cooling process. Therefore, the elemental composition measured at room temperature can be considered as an accurate estimation of the surface segregation at 1000 K. Although the adsorption of gas molecules on the surface presumably changed during the cooling process, the kinetics of atomic exchange is too slow to cause any changes in the surface composition.

Besides, it is noted that, even for the clean surface before segregation, the Cu content of the first 3 ALs is slightly lower than those of first 10 ALs and the outermost AL. This suggests that there might be a small composition inhomogeneity in the near surface region. This is probably due to preferred sputtering of Pd and the composition recovery due to the short time heat treatment during the surface cleaning process. Yet, the effect of this inhomogeneity is not affecting the conclusion regarding the surface segregation behaviour observed.

In order to quantitatively express the surface segregation behaviour of Pd-40 at.% Cu alloy, the variation of Cu content before and after annealing ($\Delta c_{Cu} = c_{Cu}^{after} - c_{Cu}^{before}$) was

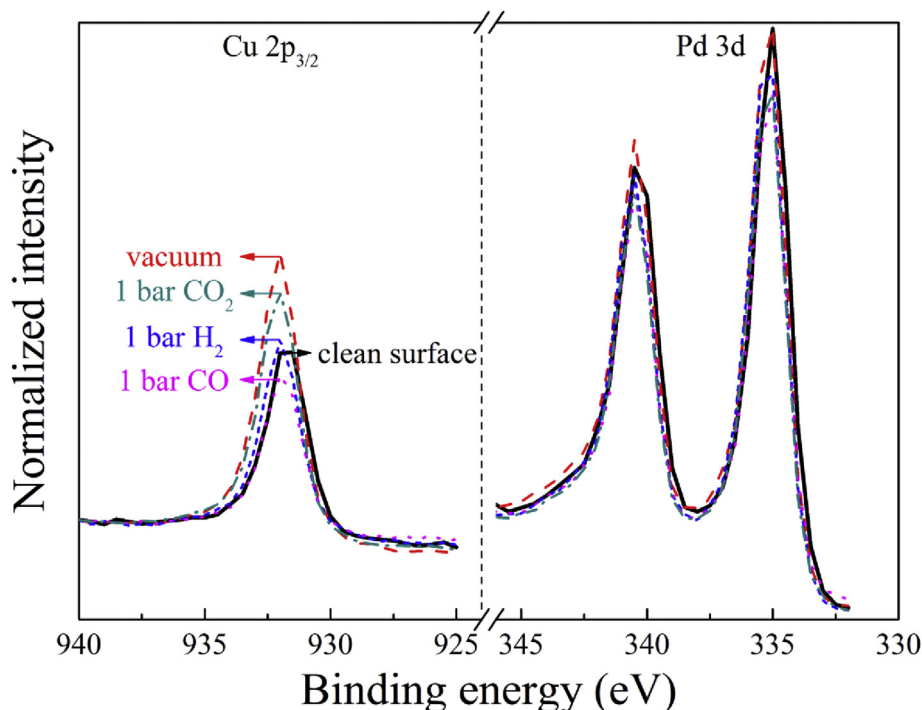


Fig. 1 – XPS spectra of Pd-40 at.% Cu alloy recorded at 45° take-off angle with respect to the sample surface before and after annealing at 1000 K in vacuum and various gas atmospheres.

calculated and summarized. As shown in Fig. 3, after annealing in vacuum and CO₂, strong Cu segregation occurs. On the other hand, after annealing in H₂ and CO, slight segregation of Cu in the outermost AL (about 1–3%) and strong segregation of Pd in the first 3 ALs region (about 4–6%) is evident. However, almost no segregation occurs on average in the first 10 ALs region (less than 1%). For each gas atmosphere applied, the segregation observed for the first 10 ALs region is always the least, while segregation in the first 3 ALs region is the strongest. This is likely due to the so-called “composition oscillation” in the surface atomic layers since surface segregation is achieved by the atomic exchange within the near

surface region [16]. It is noted that, no carbon contamination or adsorbates were detected after the sample was cooled down and transferred back to the UHV chamber. The recorded XPS spectra confirmed that no oxide was formed due to the interaction with gas atmospheres since no core-level peak shifts were observed. Hence, any effect of the adsorbates on the accuracy of XPS and LEISS measurements can be ignored. In short, the trend of surface segregation in vacuum is in good agreement with previous reported data [13,17,18], whereas the experimental results for segregation in various gas atmospheres cannot be compared due to the lack of data reported in literatures.

Since the elemental composition in the outermost AL is of most importance for the hydrogen dissociation, a thermodynamic model was developed to semi-quantitatively calculate the segregation enthalpy as well as the elemental composition

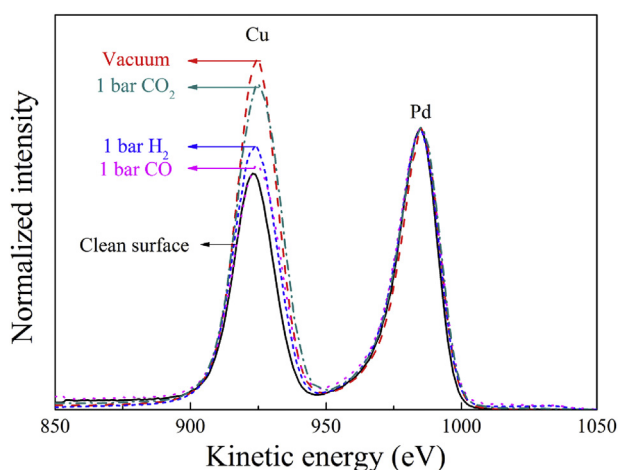


Fig. 2 – LEISS of Pd-40 at.% Cu alloy recorded with 1 keV Ar⁺ before and after annealing at 1000 K in vacuum and various gas atmospheres.

Table 1 – Cu content (atomic percentage at.%) of different depth under the surface of Pd-40 at.% Cu alloy upon segregation at 1000 K in vacuum and various gas atmospheres.

	45° XPS	15° XPS	LEISS	Calculation
	Top 10 ALs	Top 3 ALs	Outermost AL	Outermost AL
Clean surface	41.3	36.2	39.4	40.0
Vacuum	46.7	49.8	49.6	48.3
0.5 bar H ₂	41.2	29.8	42.6	37.8
0.25 bar H ₂ +0.25 bar CO	40.3	32.6	41.9	39.0
0.5 bar CO	41.6	30.9	40.3	38.4
0.5 bar CO ₂	48.5	46.1	47.6	48.3

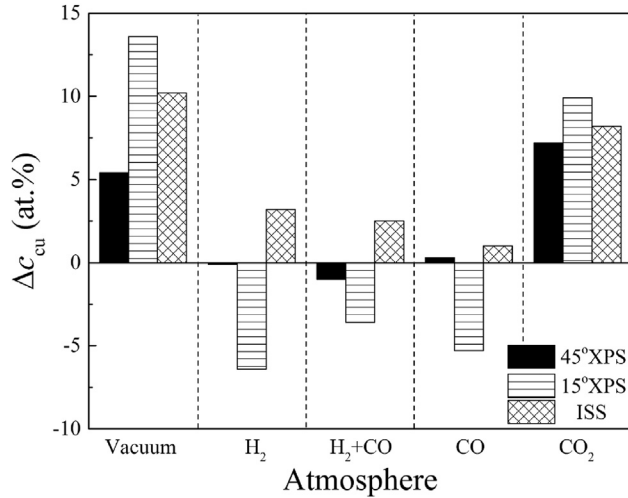


Fig. 3 – Variation of Cu content of Pd-40 at.% Cu alloy on the surface ($\Delta c_{\text{Cu}} = c_{\text{Cu}}^{\text{after}} - c_{\text{Cu}}^{\text{before}}$) before and after segregation at 1000 K in vacuum and various gas atmospheres.

in the outermost AL upon segregation. According to Wynblatt and Ku's work, surface segregation can be considered as an "atomic exchange process", during which a certain kind of atom in the outermost AL exchanges position with another kind of atom located below in the bulk of the alloy [19]. Surface energy, chemical bonding energy and the interaction with gas atmospheres are the key factors in the segregation process. Therefore, the segregation enthalpy (ΔH^{seg}) can be expressed as [12]:

$$\Delta H^{\text{seg}} = (\gamma_{\text{Cu}}\sigma_{\text{Cu}} - \gamma_{\text{Pd}}\sigma_{\text{Pd}}) + 2\omega Z_l \left(x_{\text{Cu}}^{\text{bulk}} - x_{\text{Cu}}^{\text{surf}} \right) + 2\omega Z_v \left(x_{\text{Cu}}^{\text{bulk}} - \frac{1}{2} \right) + \frac{K_A G_B (V_A - V_B)^2}{3K_A V_B + 4G_B V_A} + \theta_{\text{gas}} (\epsilon_{\text{Cu-gas}} - \epsilon_{\text{Pd-gas}}) \quad (1)$$

where γ_{Cu} and γ_{Pd} are the surface energies of the pure metals; σ_{Cu} and σ_{Pd} are the surface areas directly related to the atomic volumes V_{Cu} and V_{Pd} , respectively. Specific values can be found in Refs. [12]. The alloy parameter ω can be calculated from the experimental mixing enthalpy, representing the change of chemical bonding energy [20]. $x_{\text{Cu}}^{\text{bulk}}$ and $x_{\text{Cu}}^{\text{surf}}$ are the Cu content in the bulk and in the outermost AL. Z_l and Z_v are the number of lateral and vertical nearest neighbours. Here only the interaction between the nearest neighbour atoms is considered. K and G represent the bulk modulus and shear modulus of the pure metals. The last part of Eq. (1) represents the effect of a gas atmosphere, where $\epsilon_{\text{Cu-gas}}$ and $\epsilon_{\text{Pd-gas}}$ are the adsorption energy of the gas molecules on the corresponding metal atoms [21]. θ_{gas} is the adsorbate coverage; i.e., the number ratio between the adsorbed gas molecules and metal atoms in the outermost AL.

The Langmuir-McLean segregation equation is adopted to calculate the Cu content in the outermost AL [12]:

$$\frac{x_{\text{Cu}}^{\text{surf}}}{1 - x_{\text{Cu}}^{\text{surf}}} = \frac{x_{\text{Cu}}^{\text{bulk}}}{1 - x_{\text{Cu}}^{\text{bulk}}} \exp \left(- \frac{\Delta H^{\text{seg}}}{RT} \right) \quad (2)$$

where R is the gas constant and T is the annealing temperature (1000 K in the present research). It is noted that the contribution of configurational entropy is considered in Eq. (2), while other contributions, such as vibrational and electronic entropy, can be ignored.

In vacuum, the coverage of gaseous species, θ , is zero. As shown in Table 1, the calculation provides a Cu content of 48.3 at.% in the outermost AL, which is in good agreement with the experimental result of 49.6 at.%, showing a strong Cu segregation. In this case, the major driving force of surface segregation is surface energy reduction. Monte Carlo simulation predicted a Cu segregation of Pd-40 at.% Cu alloy in vacuum (i.e. 68 at.% Cu in the outermost AL at 900 K), which is qualitatively consistent with our result [22].

In the various gas atmospheres, θ is quite different. First, there is almost no adsorption of CO_2 on Pd and Cu at high temperatures [23]. Therefore, it is expected that the Cu content in the outermost AL upon segregation in CO_2 is similar with that in vacuum. Indeed, this is in agreement with our experimental results. On the other hand, the adsorption coverage of H_2 and CO is related to the sticking coefficient (s_T), which is a function of temperature (T) and activation energy of adsorption (E_a) [24]:

$$s_T \approx 2.7(\pm 1.2) \cdot 10^{-4} \exp \left(- \frac{2 \cdot E_a}{kT} \right) \quad (3)$$

where $E_a(\text{H}_2) \approx 0.025$ eV and $E_a(\text{CO}) \approx 0.01$ eV [25,26]. Based on previous reported data, showing that $\theta_{\text{H}} \approx 0.4$ at $T = 250$ K and $\theta_{\text{CO}} \approx 0.2$ at $T = 390$ K, the adsorption coverage at 1000 K was roughly estimated as $\theta_{\text{H}} \approx 0.32$ and $\theta_{\text{CO}} \approx 0.08$ [26]. This is

a qualitative estimation of the adsorption coverage as experimental determination is difficult at such a high temperature.

The Cu content in the outermost AL upon segregation can be calculated with Eq. (1) with gas adsorption, the results are also shown in Table 1. Qualitatively, the results of the calculation are also comparable to the experimental results. In this case, the difference of adsorption energy ($\Delta \epsilon_{\text{gas}} = \epsilon_{\text{Cu-gas}} - \epsilon_{\text{Pd-gas}}$) acts as an extra driving force of surface segregation. Quantitatively, the Cu content in the outermost AL is slightly underestimated, which is possibly due to the inaccuracy of the estimated surface adsorption coverage. Moreover, co-adsorption of H_2 and CO has already been experimentally proven, indicating that θ_{H} and θ_{CO} are additive for the H_2 and CO mixture [24]. Therefore, the Cu content in the outermost AL upon segregation in 0.25 bar H_2 +0.25 bar CO is approximately the average of those in 0.5 bar H_2 and 0.5 bar CO , as confirmed by our results. For comparison, DFT calculation confirmed the adsorbate-induced segregation of Pd

Table 2 – Calculation of surface segregation of Pd–Ag and Pd–Au alloy in vacuum, H₂ and CO (Pd_xM_{100-x}, x is the atomic percentage of the outermost atomic layer). Experimental results in vacuum from previous literatures are also shown as a comparison.

Bulk composition	Temperature	Atmosphere	Surface composition	
			Calculation	Experiments in Literature
Pd67Ag33	820 K	Vacuum $\theta_{\text{H}} = 0.32$ $\theta_{\text{CO}} = 0.08$	Pd37Ag63 Pd54Ag46 Pd52Ag48	Pd10Ag90
Pd50Au50	800 K	Vacuum $\theta_{\text{H}} = 0.32$ $\theta_{\text{CO}} = 0.08$	Pd20Au80 Pd76Au24 Pd51Au49	Pd16Au84

with CO, COH or HCO adsorption on the surface [27]. A quantitative comparison is hard to achieve due to the different surface conditions, for example the pressure of the gas atmosphere.

Except for Pd–Cu, the model has also been applied to other Pd-based alloys with various catalytic applications. Surface segregation of Pd–Ag and Pd–Au alloys were also calculated. In vacuum, the calculation predicts solute segregation at the outermost atomic layer for both Pd–Ag and Pd–Au alloys. This agrees with experimental results obtained [28,29]. However, as listed in Table 2, solute segregation can be reduced or even reversed by H₂ or CO adsorption, with adsorption coverage similar as those mentioned above for Pd–Cu alloy.

Since experimental results for segregation in various gas atmospheres are limited, our model could serve as a means to estimate surface segregation behaviour of Pd-based alloys in both vacuum and various gas atmospheres.

Conclusion

In summary, surface segregation of Pd-40 at.% Cu alloy in vacuum and various gas atmospheres were investigated with both XPS and LEISS, probing different depths below the surface. In contrast with the strong Cu segregation in vacuum, the adsorption of various gas molecules has a decisive effect on the surface composition upon segregation. Less Cu segregation was observed when exposed to H₂, CO and their mixture, while the effect of CO₂ is almost neglectable. The proposed thermodynamic model explains these phenomena semi-quantitatively by the adsorption energy as an extra driving force. The results provide basic guidelines to design novel Pd-based alloys for hydrogen separation membranes and estimate their surface stability as well as long-term performance in actual working atmospheres.

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