



The effect of adsorbed sulfur on surface segregation in a polycrystalline Pd₇₀Cu₃₀ alloy

James B. Miller^{a,b,*}, Bryan D. Morreale^a, Andrew J. Gellman^{a,b}

^aNational Energy Technology Laboratory, US Department of Energy, P.O. Box 10940, Pittsburgh, PA 15236, United States

^bDepartment of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States

ARTICLE INFO

Article history:

Received 17 February 2008

Accepted for publication 17 March 2008

Available online 23 March 2008

Keywords:

Surface segregation

Palladium–copper alloy

X-ray photoelectron spectroscopy

Low energy ion

Scattering spectroscopy

ABSTRACT

Surface segregation in alloys can be influenced by the presence of adsorbed species. In this work, the effect of adsorbed sulfur on surface segregation in a Pd₇₀Cu₃₀ alloy was studied for sulfur coverages from zero through saturation and for temperatures from 400 to 1000 K. X-ray photoemission spectroscopy (XPS) was used to determine the alloy composition in the near-surface region (~7 atomic layers) and low energy ion scattering spectroscopy (LEISS) was used to probe the composition of the topmost atomic layer of the alloy. Surface segregation was observed to depend on both the presence of adsorbed sulfur and heat-treatment history. The near-surface region of the clean alloy was enriched in Pd relative to the bulk, but the topmost atomic layer was enriched in Cu. Adsorbed sulfur caused a reversal of the Cu enrichment of the topmost surface, resulting in a top layer that contained only Pd and S atoms. Segregation reversal may be driven by the formation of thermodynamically favored Pd–S bonds at the terminating surface of the alloy.

© 2008 Elsevier B.V. All rights reserved.

1. Introduction

1.1. Surface segregation in alloys

Alloys often possess important properties that are superior to those of their pure components, and as a result, alloys are widely used as catalysts, structural materials and corrosion resistant materials. Common to all alloys is the phenomenon of surface segregation – the composition of the terminating surface differs from that of the bulk. Determination of an alloy's surface composition, and how it depends on bulk composition, temperature and the presence of adsorbed gases, is a prerequisite for understanding alloy surface chemistry.

Interactions between an alloy surface and adsorbed species are well known to effect segregation. Because of sulfur's role in corrosion and catalyst deactivation, many studies have addressed its impact on surface segregation. Sulfur has been reported to affect both the lateral distribution of alloy components at a surface [1–5] and the depth profile of alloy components into the surface [1–3,5–10]. The driving force for segregation is often formation of metal–sulfur bonds [3–5,9,10]. For example, S adsorbed on Co/Mo(110) causes reorganization of Co into islands on the surface as S interacts preferentially with Mo [1]. Ni and S have been observed to co-segregate as a “two-dimensional Ni–S compound” in both the

S–CuNi and S–AgNi systems [9,10]. Diffusion of a S impurity from the bulk to the surface of a Cu₃Au(110) single crystal is accompanied by Cu segregation to the surface to form Cu-sulfides and isolation of Au as islands [2]. In dilute alloys of Mo in Fe, S impurities co-segregate with Mo at the surface to form “two dimensional (Fe–Mo)S sulfides” [3,5]. In a report especially relevant to this work, co-segregation of Pd and a S contaminant has been demonstrated in a PdCu(110) single crystal [7].

1.2. PdCu alloy membranes for hydrogen separation applications

This work addresses surface segregation in a dense polycrystalline Pd₇₀Cu₃₀ alloy being evaluated for use as a membrane for separation of hydrogen from mixed gas streams such as those produced in coal gasification plants [11–13]. As a component of a hydrogen purification membrane, Pd dissociatively adsorbs molecular hydrogen from a mixed gas stream and allows rapid transport of the hydrogen atoms through its bulk. Recombination of hydrogen atoms on the opposite surface of the membrane and desorption of molecular hydrogen completes a sequence that effectively separates hydrogen from all other components of the mixed gas stream [14]. For “clean” hydrogen streams – those that do not contain species that poison the surface for dissociation – atomic diffusion often limits the overall hydrogen transport rates [14]. Experimental and computational research has provided a fundamental basis for understanding hydrogen transport through Pd-based membranes [11–13,15–17].

* Corresponding author. Tel.: +1 412 268 9517; fax: +1 412 268 7139.
E-mail address: jbmiller@andrew.cmu.edu (J.B. Miller).

Other components of a hydrogen-containing mixed gas stream can influence the performance of a Pd-based hydrogen purification membrane. In fossil fuel processing applications, hydrogen-containing streams usually exist at elevated temperatures – at least 600–900 K – and have significant concentrations of sulfur-containing compounds, such as H₂S. Interaction of sulfur-containing compounds with the membrane can reduce transport rates by poisoning the ability of the surface to dissociate hydrogen and/or by reacting with the membrane to form a metal-sulfide layer that impedes H-atom diffusion through the bulk [17–19].

Alloying Pd with a second component is one strategy for mitigating the effects of sulfur poisoning of Pd-based hydrogen purification membranes. Pd_xCu_{100-x} alloys have received significant attention for possible use in hydrogen purification in coal gasification applications. These studies have included the identification of membrane compositions and operating conditions that enable long term operation of Pd_xCu_{100-x} alloy membranes in H₂S-containing environments without significant degradation of their hydrogen permeance [11,17,18].

While there have been several experimental and computational studies of hydrogen diffusivity in Pd_xCu_{100-x} [11–13,15–17], relatively little is known about the surface composition of these materials in either their clean state or in the presence of hydrogen-containing gas streams. This is an important consideration; surface composition determines the catalytic activity of the surface for the first step of the separation sequence – dissociative adsorption of hydrogen. Thus, surface characterization and a fundamental understanding of segregation – both on clean alloy surfaces and in the presence of adsorbed sulfur – are key to the rational design of alloy separation membranes.

In a previous paper, we reported the results of our study of the surface composition of a clean polycrystalline Pd₇₀Cu₃₀ membrane material [20]. With its surface prepared by Ar⁺ sputtering followed by annealing at temperatures from 400 to 1000 K, the clean alloy exposed an XPS-accessible, near-surface region (~7 atom layers) enriched in Pd (relative to the bulk), but a topmost atomic layer enriched in Cu (relative to the bulk). In addition, the surface chemical activities of the Pd₇₀Cu₃₀ sample for H₂ and CO adsorption were observed to depend on sample treatment, possibly reflecting differences in the local arrangement of surface atoms in the topmost layer. In this work, we characterize segregation in Pd₇₀Cu₃₀ as a function of sulfur coverage and anneal temperature. We illustrate that adsorbed sulfur reverses the segregation trends of the clean Pd₇₀Cu₃₀ alloy, resulting in a topmost layer that contains only Pd and S atoms.

2. Experimental procedures

A polycrystalline Pd₇₀Cu₃₀ alloy was fabricated and cold-rolled to a thickness of approximately 1.0 mm by ACI Alloys, Inc. The elemental composition of the sample, measured by ion-cyclotron plasma analysis, revealed a Pd:Cu atomic ratio of 70.5:29.5, with a total residual contamination by other metals of <100 ppm by weight.

All surface analysis experiments were performed in a stainless steel ultra-high vacuum chamber with a base pressure of 1×10^{-10} Torr. The chamber is equipped with an X-ray source (VG XR3HP) and an energy analyzer (Specs PHOIBOS 150MCD) for X-ray photoemission spectroscopy (XPS). A He⁺ ion gun (Specs IQE 12/38) was used in conjunction with the energy analyzer to perform low energy ion scattering spectroscopy (LEISS). A mass spectrometer was used for temperature programmed desorption (TPD) experiments. Additional details of the apparatus have been reported elsewhere [20].

Before placement in the chamber, the Pd₇₀Cu₃₀ sample was polished with 15 and 1 μm diamond compounds. Once in the chamber, the sample was cleaned by cycles of annealing to 1000 K and Ar⁺ ion sputtering (~15 μA/cm²) at 100 K. Consistent with literature reports [21,22], we observed that Ar⁺ sputtering preferentially removes Cu atoms, creating a surface region that is depleted in Cu. Using this preparation protocol, we routinely and reproducibly prepared samples having XPS-accessible, near-surface regions with Cu atom fractions of $X_{\text{Cu}}^{\text{ns}} \leq 0.20$, where $X_{\text{Cu}}^{\text{ns}} = [\text{Cu}]/([\text{Cu}] + [\text{Pd}])$ and both [Cu] and [Pd] were determined using XPS.

The XPS experiments used Al K_α radiation, with 40 eV analyzer pass energy for detection of Cu and Pd and 100 eV pass energy for detection of sulfur. Unless noted otherwise, XPS experiments were performed at 400 K, with the sample positioned such that the analyzer collected electrons photoemitted at an angle 50° from the surface normal. For quantitative measurements of the near-surface composition, we used the ratio of the Pd 3d_{5/2} and Cu 2p_{3/2} signal intensities calibrated against signals from the same features in XP spectra obtained from clean Pd(111) and Cu(111) single crystals. For quantification of sulfur content, we scaled the S 2p photoemission signal by published sensitivity factors; this approach was verified by successful application to analysis of a sample of bulk Pd₄S. It is important to note that XPS provides an *aggregate* measure of the composition of the near-surface region. The kinetic energies of the Pd 3d_{5/2}, Cu 2p_{3/2} and S 2p photoelectrons are 1152, 555 and 1320 eV, respectively, corresponding to mean free paths of ~15 Å. Thus, at the nominal experimental geometry, >95% of the total photoemission signal originates from the top seven atomic layers of the sample, with ~40% of the total coming from the topmost atomic layer. We estimate that the reproducibility of our near-surface composition measurements, starting with a newly sputtered and heat-treated sample on each day, is within ±2%.

The LEISS experiments used 750 eV He⁺ ions specularly reflected from the sample surface at an angle ~50° from the surface normal. Low incident ion currents of ~50 nA (~1.5 × 10¹³ He⁺/cm² over the course of a single 60 s experiment) were used in order to minimize sputter damage by incident He⁺. Sulfur atoms yielded very low ion scattering signals, perhaps because of a preference for ion neutralization over elastic scattering [23]. For semi-quantitative estimates of the topmost layer S/Pd atomic composition, we compared the relative areas of S and Pd peaks to those measured for a ($\sqrt{3} \times \sqrt{3}$) R30° – S/Pd(111) surface, with $\theta_s = 0.33$. Because the area of the S feature was small and dependent on choice of background subtraction, the uncertainty in our estimate of the composition of the topmost layer of the sulfur covered Pd₇₀Cu₃₀ surface is large – about ±25%.

For the temperature programmed desorption (TPD) experiment, the sample was cooled to 100 K for exposure to H₂S. H₂S was introduced into the chamber to a partial pressure of 10⁻⁸ Torr for periods of time chosen to deliver exposures up to 0.5 L. The desorption experiment was then conducted by heating the sample at a rate of 2 K/s with the sample located within about 1 mm of the aperture to the mass spectrometer.

3. Results and discussion

3.1. Sulfur deposition

Sulfur was deposited onto the Pd₇₀Cu₃₀ alloy surface by adsorption and thermal decomposition of H₂S. Fig. 1 shows TPD spectra obtained following exposure of a surface to 0.42 L H₂S at 100 K. Prior to the TPD experiment the surface had been prepared by Ar⁺ sputtering at 100 K and annealing at 1000 K. Later, we demonstrate that the exposure required for saturation of the alloy surface with sulfur is ~0.22 L. The relative intensities of low temperature

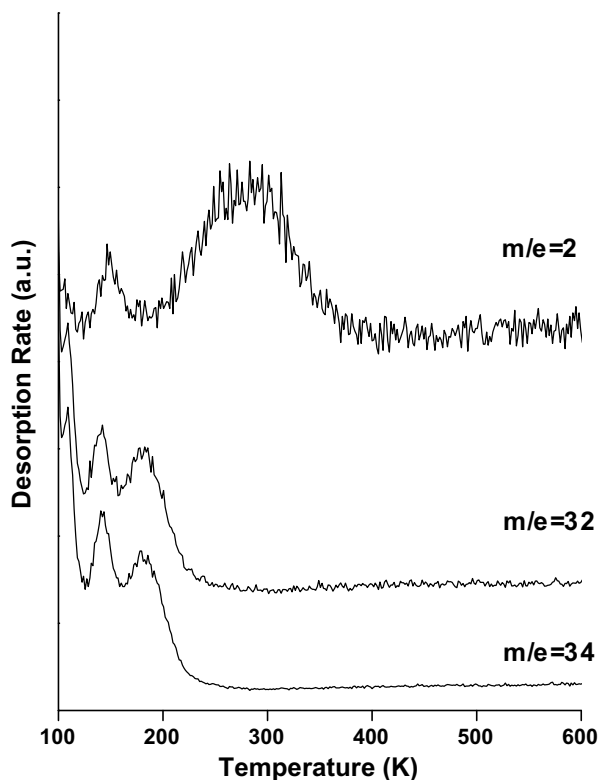


Fig. 1. Temperature programmed desorption of H₂S (0.42 L exposure at 100 K) from Pd₇₀Cu₃₀ (Ar⁺ sputtered, then annealed at 1000 K). Desorption of molecular H₂S occurs below ~200 K. Decomposition, with evolution of hydrogen, is complete by 400 K.

(<200 K) peaks for $m/e = 2, 32,$ and 34 (H₂S, H₂) are consistent with desorption of molecular H₂S. The spectrum for $m/e = 2$ (H₂) also displays a broad, high temperature peak centered at ~280 K. “Blank” TPD experiments – without adsorbed H₂S – display a small $m/e = 2$ feature at 340–360 K, presumably arising from desorption of hydrogen that had been adsorbed from the background. The $m/e = 2$ feature at 280 K in the H₂S TPD spectrum is considerably larger than that from the clean surface, and must arise from desorption of H₂ formed upon decomposition of H₂S. Significantly, H₂S decomposition is complete by 400 K.

Fig. 2 shows the S 2p region of the XP spectra obtained from the clean sample before exposure to H₂S (spectrum obtained at 400 K), after exposure to 0.42 L H₂S (spectrum obtained at 100 K), and after heating to 1000 K for the TPD experiment (spectrum obtained at 400 K). Upon heating from 100 K to 1000 K, the maximum of the S 2p peak shifts from 163.5 eV to 162.4 eV, consistent with H₂S decomposition [24,25]. The XPS data were used to estimate aggregate compositions of the near-surface region, ~7 atomic layers, of the sample. Table 1 compares sulfur content (as (S/Pd)^{ns} atom ratio) and metals content (as $X_{Cu}^{ns} = [Cu]/([Cu] + [Pd])$) of the near-surface region before H₂S adsorption, after adsorption but prior to

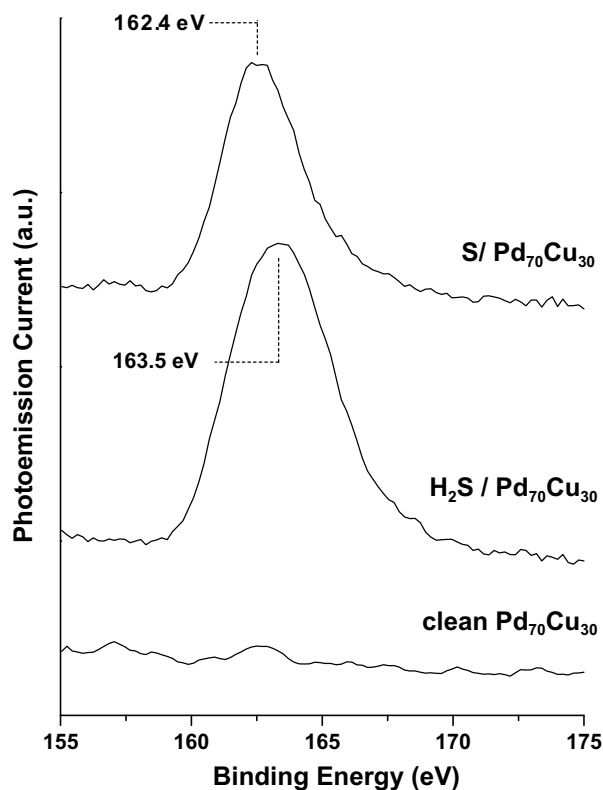


Fig. 2. S 2p region of photoelectron spectrum of Pd₇₀Cu₃₀ (Ar⁺ sputtered at 100 K and annealed at 1000 K) before H₂S exposure (bottom), after exposure (top) and after thermal desorption/decomposition of H₂S. The shift of binding energy to lower value upon heating is consistent with H₂S decomposition. Emission angle in these experiments is 50° from the surface normal.

decomposition, and after decomposition by annealing the surface to 1000 K. Before H₂S adsorption, the sample’s near-surface contains no measurable sulfur: (S/Pd)^{ns} < 0.01. Upon exposure to H₂S, the sulfur concentration grows considerably, to (S/Pd)^{ns} = 0.13. Heating the sample to 1000 K during TPD causes the sulfur concentration to decrease to (S/Pd)^{ns} = 0.09. The signal decrease is consistent with our observation that some H₂S desorbs at low temperatures during the TPD experiment (Fig. 1).

Table 1 also illustrates that adsorption of molecular H₂S onto the sample surface at 100 K does not change the relative concentrations of Cu and Pd in the near-surface region. However, decomposition of H₂S during TPD causes the Cu content of the near-surface region to decrease; this is our first evidence of the impact of adsorbed sulfur on segregation at the Pd₇₀Cu₃₀ alloy surface.

The amount of sulfur deposited onto the Pd₇₀Cu₃₀ alloy surface can be systematically changed by varying its exposure to H₂S. To illustrate this point, we exposed the clean alloy surface, which had been annealed at 1000 K, to H₂S at 400 K, a temperature at which decomposition and hydrogen desorption would be expected to occur. The S 2p binding energies on surfaces modified with H₂S in this manner are the same as those of prepared by low tempera-

Table 1

Compositions of the near-surface region of Pd₇₀Cu₃₀ during adsorption and decomposition of H₂S, as estimated from XP spectra

	Clean surface (spectra collected at 400 K)	After exposure to 0.42 L H ₂ S at 100 K (spectra collected at 100 K)	After heating to 1000 K (spectra collected at 400 K)
(S/Pd) ^{ns} (atom ratio)	<0.01	0.13 ± 0.01	0.09 ± 0.01
$X_{Cu}^{ns} = Cu/(Pd + Cu)$	0.23 ± .01	0.22 ± 0.01	0.19 ± 0.01

Compositions are aggregate estimates for the near-surface region, ~7 atomic layers.

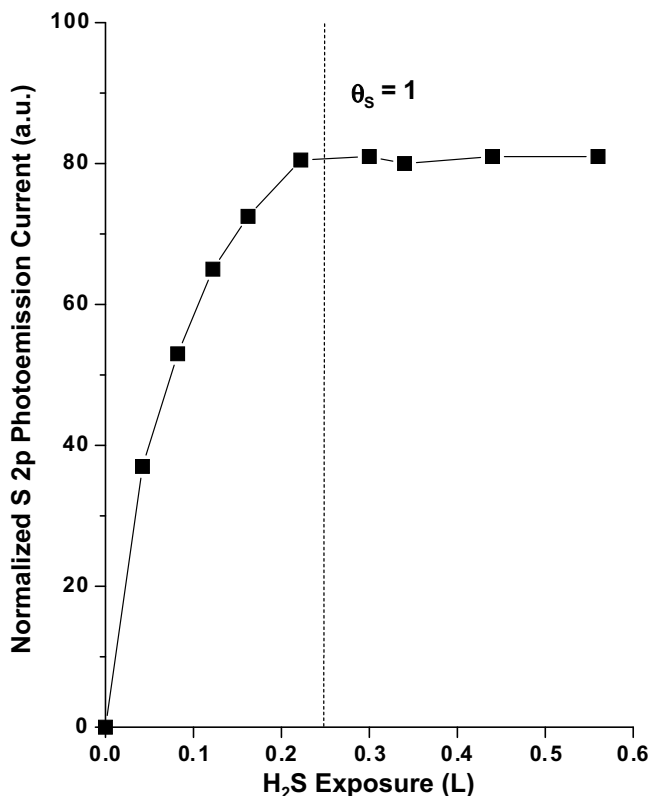


Fig. 3. S 2p photoemission signal for Pd₇₀Cu₃₀ (Ar⁺ sputtered at 100 K and annealed at 1000 K) as a function of H₂S exposure at 400 K. Saturation ($\theta_s = 1.0$) occurs at 0.22 L; sub-saturation coverages are reproducibly obtained by selecting exposures less than 0.22 L.

ture H₂S adsorption followed by heating to 1000 K. As shown in Fig. 3, the S 2p signal increases with H₂S exposure and saturates at ~0.22 L. Subsaturations, expressed as θ_s , the fraction of the saturation sulfur coverage, were obtained reproducibly by selecting exposures less than 0.22 L.

3.2. Pd and Cu content of the near-surface region

The Pd₇₀Cu₃₀ alloy sample, cleaned by room temperature Ar⁺ sputtering at 100 K followed by annealing at 300 K, was exposed to H₂S at 400 K to generate sulfur coverages of $\theta_s = 0.33, 0.67$ and 1.0 (relative to the saturation coverage). For each sulfur exposure – including the “clean” state ($\theta_s = 0.00$) – the sample was annealed for 30 min at 400, 600, 800, and 1000 K. At all anneal temperatures, the near-surface composition, measured by XPS, achieved steady state within 30 min; the relative magnitudes of Pd and Cu signals typically changed by less than 1% upon increasing the annealing time from 20 to 30 min at these temperatures.

The near-surface metal compositions of the sample, $X_{Cu}^{ns} = [Cu]/([Cu] + [Pd])$, measured by XPS, appear in Fig. 4 as functions of anneal temperature for different sulfur coverages. The top curve, representing the clean sample, reproduces the results that we reported previously [20]. Sputtering preferentially removes Cu atoms to create a Pd-rich near-surface region, with $X_{Cu}^{ns} \sim 0.16$, significantly lower than the value of $X_{Cu} = 0.30$ in the bulk. When the clean, sputtered sample is annealed at temperatures between 600 and 1000 K, Cu migrates from the bulk into the near-surface region; the extent of Cu migration depends on the anneal temperature. However, despite Cu migration to repopulate the near-surface region, the near-surface remains Pd-rich at all anneal temperatures. As noted in our previous report [20], compositions of the clean sam-

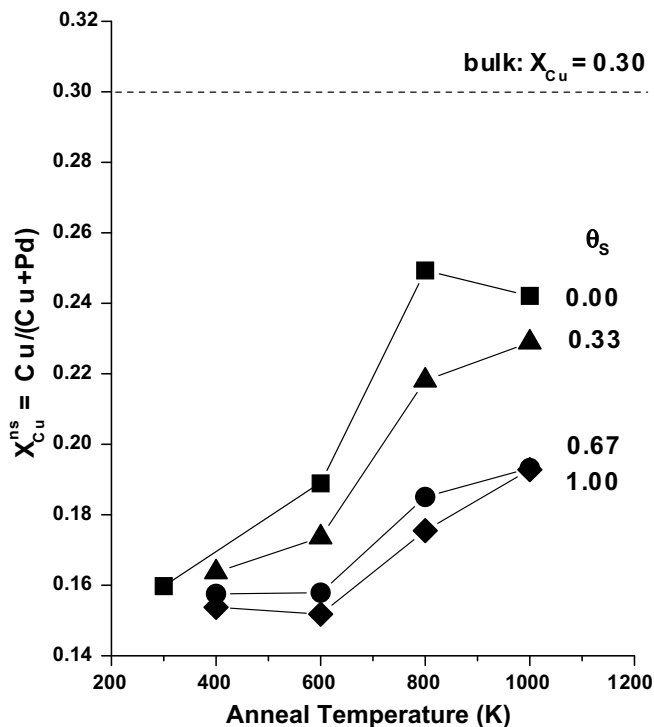


Fig. 4. Near-surface region composition of the Pd₇₀Cu₃₀ alloy as functions of sulfur coverage, θ_s , and anneal temperature. The near-surface of the clean sample is Cu-depleted relative to the bulk ($X_{Cu} = 0.30$) at all anneal temperatures. Adsorbed sulfur increases the extent of Cu-depletion at all coverages and anneal temperatures. Emission angle in these experiments is 50° from the surface normal.

ple measured for anneal temperatures of 800 and 1000 K probably represent near-surface regions that are in thermodynamic equilibrium with the bulk; compositions measured at 600 K and below may be determined by slow diffusion kinetics.

Sulfur adsorption causes significant changes to the composition of the near-surface region. As illustrated in Fig. 4, adsorbed sulfur reduces the extent to which Cu repopulates the near-surface region upon annealing – X_{Cu}^{ns} for the sulfur-treated samples are lower than those of the clean surface at all temperatures. Furthermore, at each anneal temperature, X_{Cu}^{ns} decreases with increasing sulfur coverage. Significantly, even at low temperatures adsorbed sulfur influences the composition of the near-surface region – X_{Cu}^{ns} measured immediately after decomposition of H₂S on the alloy surface at 400 K decreases with increasing sulfur coverage.

Angle-resolved XPS experiments provide important insight into the composition gradients that exist within the near-surface region. As the angle between the analyzer and the surface-normal approaches 90° (at which point the analyzer is parallel to the surface), the analyzer preferentially samples electrons photoemitted from the topmost atomic layers. Fig. 5 shows selected results of angle-resolved XPS experiments performed on the same samples characterized by the “single-point (emission measured at 50° from surface normal)” XPS experiments of Fig. 4. The dotted curve with open square symbols near the bottom of Fig. 5 shows results for the clean sample after Ar⁺ sputtering at 100 K, but before high temperature annealing – the common starting point for all other experiments. Sputtering preferentially removes Cu atoms, leaving behind a fairly uniform, Pd-rich near-surface region with no concentration gradient in the near-surface region. Upon annealing at 800 K, Cu atoms migrate from the bulk of the clean sample to repopulate the surface region (compare open squares and filled squares in Fig. 5). Note that, upon annealing at 800 K, X_{Cu}^{ns} increases with increasing emission angle; at the highest angle, it exceeds the

Cu composition of the bulk. Consistent with the low energy ion scattering measurements that we reported previously [20], this observation suggests that the topmost atomic layer(s) of the clean sample annealed at 800 K are Cu-rich relative to the bulk.

The remaining curves in Fig. 5 illustrate how $X_{\text{Cu}}^{\text{ns}}$ responds to deposition of different amounts of sulfur, followed by annealing at 800 K. As noted earlier, adsorbed sulfur reduces the extent to which Cu repopulates the sputter-depleted near-surface region upon annealing. At the lowest sulfur coverage studied, $\theta_s = 0.33$, values of $X_{\text{Cu}}^{\text{ns}}$ are below those measured for the clean surface; as sulfur coverage increases to saturation, $X_{\text{Cu}}^{\text{ns}}$ decreases even further. The angle resolved experiments reveal that high sulfur coverages cause the measured value of $X_{\text{Cu}}^{\text{ns}}$ to decrease with increasing emission angle. This observation suggests that significant Pd enrichment within the topmost layers of the surface region occurs as a result of sulfur adsorption. Thus, adsorbed sulfur induces a segregation reversal at the topmost surface – a switch from a Cu-rich topmost surface for the clean alloy to a Pd-rich topmost surface in the presence of adsorbed sulfur.

3.3. Sulfur content of the near-surface region

The amount and location of sulfur within in the near-surface region are important factors in understanding the effect of sulfur on segregation at the $\text{Pd}_{70}\text{Cu}_{30}$ alloy surface. Fig. 6 displays the results of angle-resolved XPS analysis of the S-saturated alloy surface for S/Pd ratio after annealing at various temperatures. The most compelling feature of the curves is their steep slope as the emission angle approaches 90° – at which the technique is sensitive to the topmost atomic layers. The results suggest that the sulfur atoms are located at or very near the topmost surface of the alloy surface

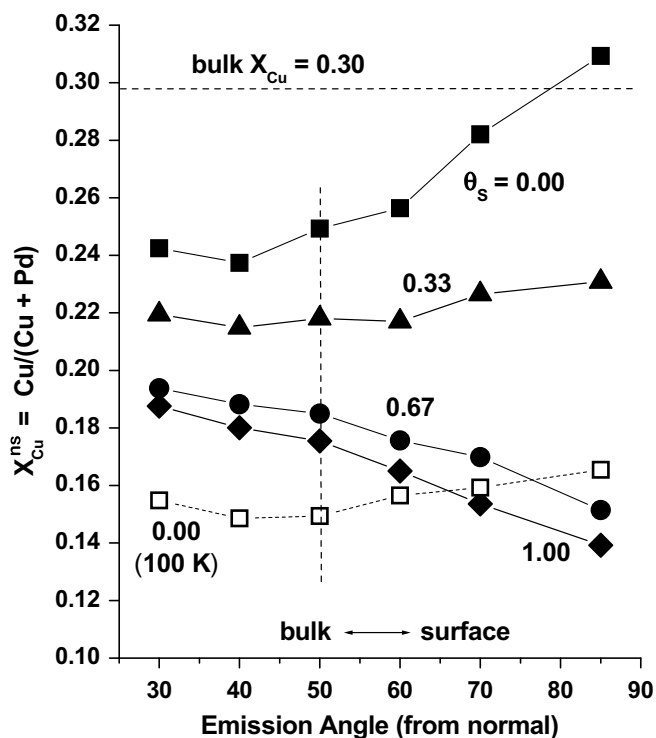


Fig. 5. Angle-resolved XPS measurements of the clean and sulfur-treated sample after annealing at 800 K. Increasing surface sulfur coverage leads to lower $X_{\text{Cu}}^{\text{ns}}$ at all emission angles and changes in the concentration profile shape – from rising $X_{\text{Cu}}^{\text{ns}}$ near the top layer (positive slope) on the clean surface to falling $X_{\text{Cu}}^{\text{ns}}$ near the surface (negative slope). The dotted curve is for a clean sample that was sputtered at 100 K, but not annealed. The nominal emission angle is 50° from surface the normal (dotted vertical line).

– adsorbed sulfur is not diffusing into the surface to any significant extent. This behavior is consistent with the behavior of bulk sulfur contaminants which often segregate to the surface of alloys such as $\text{Pd}_x\text{Cu}_{100-x}$ [2,3,5,7].

The actual values of S/Pd are also of interest. We first note that the values of the S/Pd ratio at 1000 K are slightly lower at all emission angles, suggesting partial desorption of S at this temperature. Consistent with this observation, our H_2S thermal desorption spectra exhibit a small increase in the $m/e = 32$ desorption signal between 900 and 1000 K (not shown in Fig. 1); desorption features in this temperature range have been reported during the TPD of S_2 adsorbed on Pd (1 1 1) [26]. In addition, S/Pd ratios near the topmost surface suggest a surface stoichiometry that is rich in sulfur relative to Pd_4S , a common bulk corrosion product in Pd-based separation membranes. The highest measured S/Pd ratio, 0.37, corresponds to “ $\text{Pd}_{2.7}\text{S}$ ” stoichiometry. However, because sub-surface atomic layers still contribute to the XPS signal at 85° emission angle, it is possible that the top layer has even higher S/Pd ratio.

3.4. Composition of the topmost atomic layer

Low energy ion scattering spectroscopy has been used to determine the composition of the topmost layer of the sulfur modified $\text{Pd}_{70}\text{Cu}_{30}$. Fig. 7 displays a series of LEIS spectra of the alloy surface that was exposed to H_2S to achieve $\theta_s = 1$, and then annealed for 30 min at 400, 600, 800, and 1000 K. For comparison (dotted line), we show the LEIS spectrum of a clean $\text{Pd}_{70}\text{Cu}_{30}$ surface that had been annealed at 1000 K. Note that the spectra obtained from the S-treated sample are dominated by a single feature which corresponds to Pd. The Pd feature grows as the annealing temperature increases, possibly due to decreasing surface roughness [27,28], which can attenuate the LEIS yield. Notably absent from the

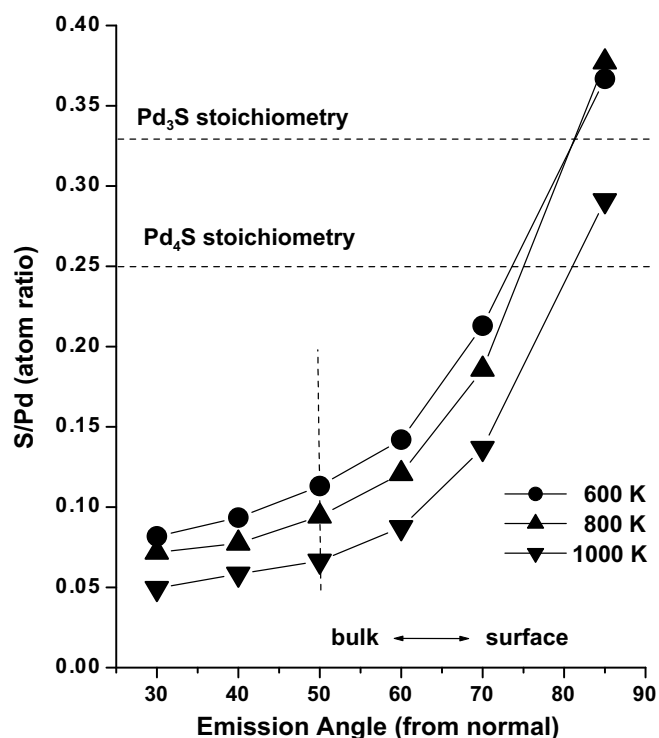


Fig. 6. Angle-resolved XPS measurement of the sulfur content of saturated ($\theta_s = 1.00$) samples as a function of anneal temperature. As emission angle approaches 90° , the technique becomes more sensitive to the outermost atomic layers. Sulfur is located at – or at least very near – the topmost layer. The sulfur concentration near the top layer is greater than in Pd_3S stoichiometry. The nominal emission angle is 50° from the surface normal (dotted vertical line).

spectra of the surfaces with adsorbed sulfur are features assignable to Cu. This result is consistent with the angle-resolved XPS analysis of $X_{\text{Cu}}^{\text{ns}}$ (Fig. 5), which suggests significant Pd enrichment in the topmost atomic layers of samples when modified by adsorbed sulfur. Thus, our LEISS results provide supporting evidence for sulfur-induced segregation reversal.

At all anneal temperatures, small features assignable to S are observed in the LEIS spectra. The inset in Fig. 7 shows an enlargement of the S-region of the LEIS spectrum of the sample annealed at 800 K. The small size of the feature may reflect a preference for He^+ to neutralize, rather than scatter elastically, during its interaction with adsorbed sulfur [23]. For a semi-quantitative estimate of surface stoichiometry, we compared the relative S and Pd peak areas to those measured for $(\sqrt{3} \times \sqrt{3}) \text{R}30^\circ - \text{S}/\text{Pd}(111)$, with $\theta_{\text{S}} = 0.33$. Based on this comparison, we estimate that the stoichiometry of the topmost layer of the alloy surface with $\theta_{\text{S}} = 1.0$ corresponds to “ $\text{Pd}_{1.8 \pm 0.5}\text{S}$ ” after annealing to 800 K; surface stoichiometries at the other anneal temperatures do not differ significantly from this value. The uncertainty of this estimate is high because the areas of the sulfur feature are small and rather sensitive to peak-fitting and background-subtraction protocols. However, our estimate is consistent with the angle-resolved XPS analysis of the near surface, which suggests that the topmost layer is sulfur-rich relative to a stoichiometry of “ $\text{Pd}_{2.7}\text{S}$ ”.

3.5. Pd-S bond formation as a driving force for segregation

In a previous paper we reported that, for the clean $\text{Pd}_{70}\text{Cu}_{30}$ alloy, temperatures of ~ 600 K were required to initiate diffusion of Cu atoms from the bulk to repopulate the sputter-depleted near-sur-

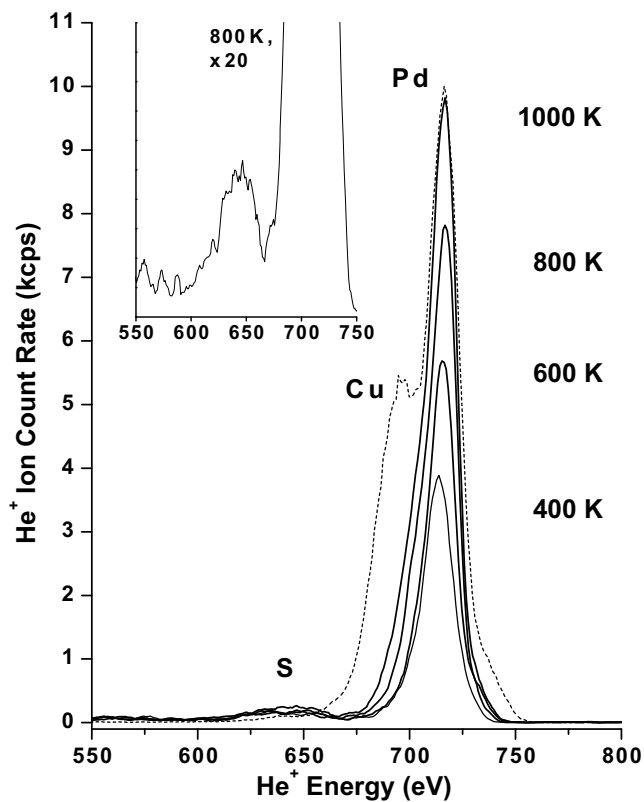


Fig. 7. LEIS spectra of $\text{Pd}_{70}\text{Cu}_{30}$ alloy, with $\theta_{\text{S}} = 1$, as a function of anneal temperature. The dotted line shows a spectrum of the clean alloy annealed at 1000 K. At all anneal temperatures, the spectra of the sulfur-treated sample are dominated by a single feature, assignable to Pd; Cu is not detected. The inset shows an enlargement of the sulfur region of the sample annealed at 800 K. A small feature, corresponding to topmost surface stoichiometry of “ $\text{Pd}_{1.8 \pm 0.5}\text{S}$ ”, is observed.

face, but that near-surface regions in equilibrium with the bulk were obtained only after annealing at 800 K or higher [20]. Over the entire range of anneal temperatures studied, 400–1000 K, the clean alloy surface displayed a Pd-rich near-surface region, but a topmost surface that was Cu-rich relative to the bulk. Analysis of the measured topmost surface compositions (at 800 K and above) using a simple, regular-solution thermodynamic model, allowed us to estimate ΔG_{S} , the Gibbs free energy of Cu segregation to the terminating surface of the alloy. Our estimate of $\Delta G_{\text{S}} = -8.7$ kJ/mol [20], was comparable to the surface tension (surface free energy) difference between the Cu and Pd pure components, -8.3 kJ/mol [20,29,30], suggesting that the surface tension difference is the primary driver of segregation in the clean alloy [20].

Deposition of sulfur onto the alloy surface causes significant changes in segregation. Results from angle-resolved XPS and LEISS illustrate that adsorbed sulfur resides at the top surface layer(s) of the alloy, without significant diffusion into the bulk. This is not a surprising result given the numerous reports of contaminant sulfur migrating to the surfaces of pure metals and alloys during annealing [2,3,5,7]. The topmost layer has a stoichiometry that is richer in S than Pd_4S , a bulk compound frequently observed during high-temperature, high $\text{P}_{\text{H}_2\text{S}}$ sulfidation of Pd; our best estimate of the surface stoichiometry is “ $\text{Pd}_{1.8}\text{S}$ ”. However, despite localization near the terminating surface, sulfur exerts an influence on composition throughout the XPS-accessible, near-surface region – at all anneal temperatures, Cu concentrations in near-surface region of the sulfur-treated samples are lower than in the clean alloy. LEISS measurements of the top layer composition illustrate that depletion of the near-surface Cu is accompanied by complete displacement of Cu atoms by Pd in the topmost layer to give a topmost layer that consists of only Pd and S atoms – segregation reversal compared to the clean alloy surface.

The impact of adsorbed sulfur on the composition of the near-surface region occurs immediately upon decomposition of adsorbed H_2S at 400 K, suggesting that there is a strong driving force for atomic redistribution. The likely driver is formation of thermodynamically favored Pd–S bonds at the surface. The Pd–S surface species is probably best described as S chemisorbed on Pd, although we note that the term “two dimensional surface sulfide” has also been used [3,5,9,10,31–33], often, but not exclusively, within the context of sulfur that has segregated from the bulk of a metal or alloy to its surface [3,5]. In the Pd–S system, a two-dimensional sulfide, based on square-planar PdS , has been proposed as a model for the Pd–S species generated by S_2 adsorption onto $\text{Pd}(111)$ [26].

Table 2 compares the free energies of formation of bulk Pd and Cu-sulfides and the surface free energy driving force for Cu surface segregation, illustrating a clear preference for the formation of Pd sulfides over Cu sulfides. At the terminating surface, sulfur-metal adsorption energies (2D surface sulfides) are typically larger than those of the sulfur–metal bonds in corresponding bulk (3D) sulfides [31–33] – this is consistent with our observation that the monolayer of adsorbed sulfur *does not* migrate into the bulk of the alloy. Furthermore, because the energies of formation of me-

Table 2

Free energies of segregation [20,29,30] and formation of bulk Cu-sulfides [34] and Pd sulfides extrapolated from [35]

	ΔG_{300}^0
Surface segregation of Cu	-8.7 kJ/mol metal
PdS	-118 kJ/mol S
$\text{Pd}_{16/7}\text{S}$	-151 kJ/mol S
Pd_3S	-147 kJ/mol S
Pd_4S	-156 kJ/mol S
Cu_2S	-86.2 kJ/mol S
CuS	-49.0 kJ/mol S

tal–S bonds in the 2D and 3D sulfides are highly correlated [31–33], Pd–S, and not Cu–S, is expected to be the energetically favored surface species in the S–Pd₇₀Cu₃₀ system. Thus, diffusion of Pd from the bulk through the surface region to form a thermodynamically favored Pd–S surface species provides a plausible explanation for the segregation reversal observed upon adsorption of sulfur onto the alloy surface.

4. Conclusions

A polycrystalline Pd₇₀Cu₃₀ alloy, Ar⁺ sputtered at 100 K and annealed at temperature in the range 400–1000 K, exhibits a topmost atomic layer that is Cu-rich relative to the bulk, but an XPS accessible near-surface region (~7 atom layers) that is Pd-rich relative to the bulk. Sulfur, deposited onto the surface of the alloy by thermal decomposition of adsorbed H₂S, causes segregation reversal. At all sulfur coverages ($\theta_s = 0.33, 0.67$ and 1.0) and heat-treatment temperatures between 400 and 1000 K, the topmost layer of the alloy surface with adsorbed sulfur contains no Cu atoms and the surface region becomes even more enriched in Pd than the clean alloy surface. The driving force for segregation reversal is probably formation of thermodynamically favored Pd–S bonds at the terminating surface of the alloy.

Acknowledgement

This research effort was performed in support of the DOE National Energy Technology Laboratory under Contract 41817M203841817M2000.

References

- [1] D.A. Chen, C.M. Friend, *Surface Science* 371 (1997) 131.
- [2] Y. Huang, J.M. Cowley, *Surface Science* 328 (1995) 277.
- [3] A. Rolland, M. Montagono, J. Cabane, *Surface Science* 352–354 (1996) 206.
- [4] J.A. Rodriguez, M. Kuhn, J. Hrbek, *Journal of Physical Chemistry* 100 (1996) 15494.
- [5] A. Rolland et al., *Applied Surface Science* 108 (1997) 425.
- [6] B.W. Busch, T. Gustafsson, *Applied Physics Letters* 74 (23) (1999) 3564.
- [7] J. Loboda-Cackovic, *Vacuum* 48 (11) (1997) 913.
- [8] E.C. Viljoen, C. Uebing, *Surface Science* 410 (1998) 123.
- [9] M. Pierantoni, B. Aufrey, F. Cabane, *Journal of Physics Colloquim* 46 (C4) (1985) 517.
- [10] B. Aufray, A. Rolland, P. Gas, *Surface Science* 178 (1–3) (1986) 872.
- [11] B.H. Howard et al., *Journal of Membrane Science* 241 (2) (2004) 207.
- [12] P. Kamakoti et al., *Science* 307 (5709) (2005) 569.
- [13] B.D. Morreale et al., *Journal of Membrane Science* 212 (1–2) (2003) 87.
- [14] S.N. Paglieri, J.D. Way, *Separation and Purification Methods* 31 (1) (2002) 1.
- [15] P. Kamakoti, D.S. Sholl, *Journal of Membrane Science* 225 (1–2) (2003) 145.
- [16] P. Kamakoti, D.S. Sholl, *Physical Review B* 71 (1) (2005).
- [17] B.D. Morreale et al., *Journal of Membrane Science* 241 (2) (2004) 219.
- [18] B.D. Morreale, *The influence of H₂S on palladium and palladium–copper alloy membranes*, Chemical Engineering, University of Pittsburgh, 2006.
- [19] B.D. Morreale et al., *Industrial and Engineering Chemistry Research* 46 (19) (2007) 6313.
- [20] J.B. Miller, C. Matranga, A.J. Gellman, *Surface Science* 602 (2008) 375.
- [21] R.H. Bergmans et al., *Surface Science* 345 (1996) 303.
- [22] J. Loboda-Cackovic, M.S. Mousa, J.H. Block, *Vacuum* 46 (2) (1995) 89.
- [23] Y. Luo et al., *Journal of Vacuum Science and Technology A* 18 (2) (2000) 438.
- [24] Q. Wu, B.V. Yakshinskiy, T.E. Madey, *Surface Science* 523 (2003) 1.
- [25] C.D. Wagner, et al., *NIST X-ray photoelectron spectroscopy database (NIST Standard Reference Database 20, Version 3.4)*, National Institute of Standards and Technology, US Department of Commerce, 2000.
- [26] C.H. Patterson, R.M. Lambert, *Surface Science* 187 (1987) 339.
- [27] H.H. Brongersma et al., *Surface Science Reports* 62 (2007) 63.
- [28] H. Neihus, W. Heiland, E. Taglauer, *Surface Science Reports* 17 (4–5) (1993) 213.
- [29] F.R. deBoer et al., *Cohesion in Metals*, North-Holland, Amsterdam, 1988.
- [30] H.L. Skriver, N.M. Rosengaard, *Physical Review B* 46 (11) (1992) 7157.
- [31] J. Benard et al., *Adsorption on Metal Surface: An Integrated Approach*, Studies in Surface Science and Catalysis, vol. 13, Elsevier, Amsterdam, 1983.
- [32] J. Benard et al., *Surface Science* 88 (1979) L35.
- [33] J. Cabane, F. Cabane, *Equilibrium segregation in interfaces*, in: J. Nowotny (Ed.), *Interface Segregation and Related Processes in Materials*, Trans Tech Publications Ltd., Zurich, 1991.
- [34] C.T. Anderson, *Journal of the American Chemical Society* 54 (1932) 107.
- [35] J.R. Taylor, *Metallurgical Transactions B* 16B (1985) 143.