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Surface segregation in a polycrystalline $Pd_{70}Cu_{30}$ alloy hydrogen purification membrane

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Abstract

X-ray photoelectron spectroscopy (XPS) and low energy ion scattering spectroscopy (LEISS) have been used to study the effects of various surface preparations and thermal treatments on the composition of the near-surface region (~7 atomic layers) and the topmost atomic layer of a polycrystalline $Pd_{70}Cu_{30}$ alloy. Palladium enrichment (relative to the bulk composition) is observed in the XPS-accessible near-surface region, but copper enrichment is observed in the topmost atomic layer. At temperatures above ~800 K, where the bulk, the near-surface region and the topmost atomic layer are likely in thermodynamic equilibrium, segregation to the top layer can be described in terms of a simple thermodynamic model. Temperature programmed desorption (TPD) of H_2 and CO from the annealed surfaces illustrates the impact of segregation and atomic distribution in the top layer on surface chemical activity.

Keywords: Low energy ion scattering (LEIS); X-ray photoelectron spectroscopy (XPS); Surface segregation; PdCu alloy; Separation membrane

1. Introduction

Metal alloys often display desirable properties that are superior to those of their individual components, accounting for their wide-spread use in structural, corrosion-control, and catalytic applications. An important characteristic of all alloys is that segregation of one component to the alloy surface causes the surface composition to differ significantly from the bulk composition. Thus, determining the surface composition of an alloy is the first step in understanding its surface chemistry. Complicating this determination is the fact that segregation depends on temperature, bulk alloy composition, the concentration of bulk impurities, the presence of adsorbed gases, and many other factors.

Our work addresses surface segregation in a dense polycrystalline palladium-copper alloy being evaluated as a membrane for the separation of hydrogen from gas streams generated by coal gasification [1–3]. Membranes that are selectively permeable to hydrogen offer a simple and effective solution for separating high purity hydrogen from mixed gas streams [4,5]. Current approaches typically employ palladium (Pd) because of its unique ability to dissociatively adsorb molecular H_2 on its surface and the very high diffusivity of hydrogen atoms through its bulk [5]. Thus, with H_2 as a component of a mixed gas stream, hydrogen—in atomic form—selectively penetrates a dense Pd membrane. On the opposite side of the membrane, H-atoms recombine and desorb as H_2, resulting in the highly selective separation of H_2 from all other components of the gas stream [5]. At temperatures typically encountered in hydrogen purification applications, the dissociative adsorption and associative desorption steps are rapid and it is the bulk diffusion of H-atoms through the membrane that limits the net rate of hydrogen transport.

In practical implementations as a membrane material for hydrogen purification, pure palladium suffers from several limitations, including high cost, marginal mechanical

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strength, and instability in oxidizing and sulfur-containing environments [6,7]. The presence of sulfur in the gas phase can result in contamination of the membrane surface to the point at which it will no longer dissociatively adsorb H_2. One approach to overcoming these limitations is to alloy Pd with other metals; such PdCu alloy membranes are being evaluated for applications in coal gasification. At conditions of H_2S exposure that cause ~80% reduction of the hydrogen flux through a pure palladium membrane, it has been reported that there is less than 10% reduction of the hydrogen flux through $Pd_{70}Cu_{30}$ and $Pd_{45}Cu_{55}$ membranes [1,6,7].

Although several experimental and computational groups have studied hydrogen diffusivity in PdCu alloys [1–3,7–9], little is known about the surface compositions of these materials. This is an important issue because surface composition influences the rate of the dissociative H_2 adsorption step. For an alloy membrane with a surface composition that is unfavorable for H_2 dissociation, the dissociation step could become rate limiting in the hydrogen transport process. In addition to understanding segregation at the clean alloy surface, it is important to understand how common gas stream impurities such as H_2S or CO affect the surface composition of these alloys.

Surface segregation in alloys has received significant attention from both experimental and computational research groups [10–19]. The PdCu system itself has been studied to some degree. Loboda-Cackovic and co-workers used Auger electron spectroscopy (AES) and temperature programmed desorption (TPD) of CO to show that a $Pd_{50}Cu_{50}(110)$ single crystal has compositions in the near-surface region and top atomic layer that differ from the bulk composition. Segregation to the $Pd_{50}Cu_{50}(110)$ surface depends on the crystal's preparation history, with segregation of Cu to the surface being favored upon annealing to temperatures above ~550 K [12,13]. Newton and co-workers report similar results for a $Pd_{15}Cu_{85}(110)$ single crystal, which exposes a purely Cu top layer as determined by low energy ion scattering spectroscopy (LEISS) [14]. Bergmans and co-workers also used LEISS to study a $Pd_{15}Cu_{85}(110)$ single crystal [15]; they observed a top layer that was only slightly enriched in Cu and a second layer that was significantly enriched in Pd. Theoretical studies of the PdCu system with low Cu concentrations suggest an oscillatory depth profile, with top layers that are either Pd-rich [16] or Cu-rich [17] relative to the bulk. Other theorists predict that segregation patterns vary significantly with bulk composition [18,19].

In this paper we report results for our study of surface segregation in a polycrystalline $Pd_{70}Cu_{30}$ (bulk composition, $X_{\mathrm{Cu}}^{\mathrm{bulk}} = 0.3$) alloy used as a membrane for hydrogen purification. We chose this composition both because of its relevance to the purification application and because, over the range of temperatures used in this work, the bulk alloy exists in a single phase, a disordered FCC solid solution [20–22]. We have used X-ray photoelectron spectroscopy (XPS) to determine how the composition of the alloy's near-surface region ($X_{\mathrm{Cu}}^{\mathrm{ns}}$) varies as a function of preparation history – sputtering and annealing – and LEISS to determine how the composition of the topmost atomic layer ($X_{\mathrm{Cu}}^{\mathrm{top}}$) responds to temperature cycling. We analyze the observed segregation with a simple thermodynamic model which reproduces our experimental results at temperatures above ~800 K. Using temperature programmed desorption (TPD) of CO and H_2, we have studied the impact of segregation on the alloy surface chemistry, and thereby probe the local ordering of Cu and Pd within the top layer.

2. Experimental procedures

A PdCu alloy, with a composition that is nominally 70 atomic percent Pd and 30 atomic percent Cu, was fabricated and cold-rolled to a thickness of approximately 1.0 mm by ACI Alloys, Inc. Elemental analysis of the sample by inductively-coupled plasma-mass spectrometry 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 a monochomated X-ray source (Thermo VG Scientific), a He^+ ion gun for LEISS (Specs IQE 12/38), an energy analyzer (Specs PHOIBOS 150MCD), and a mass spectrometer detector for temperature programmed desorption (TPD) experiments. In addition, the chamber has an ion gun for sputter cleaning of the sample and an evaporative source for depositing Cu on the sample surface. The sample was attached to an x, y, z, θ manipulator by 0.63 mm Ta lead wires spot welded to its edges and was cooled by liquid nitrogen. The Ta wires provide both mechanical support and electrical/thermal contact to the sample, allowing control of its temperature over the range 80–1100 K.

Before placement in the chamber, the sample was polished with 15 and 1 μ diamond compounds. Once in the chamber, the sample was cleaned by cycles of annealing to 1000 K and Ar^+ ion sputtering (~15 μA/cm^2) at 300 K. Consistent with literature reports [12,15], 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 repeatably prepared samples having XPS-accessible near-surface regions with Cu atom fractions of $X_{\mathrm{Cu}}^{\mathrm{ns}} \leqslant 0.22$.

The XPS experiments used Al Kα radiation and 100 eV analyzer pass energy. The analyzer collected electrons photoemitted at an angle of 30° from the surface normal. We performed all XPS experiments at 400 K, a temperature at which the composition is stable over the time scale of the measurement (~3 min). For example, in order to determine the composition as a function of time during annealing at 800 K, we first annealed the sample at 800 K for a period of time, cooled it to 400 K to obtain an XP spectrum, and then heated it back to 800 K for an additional period of time before cooling to 400 K for the next XPS measurement. We note that, for a sample that had reached steady-state near-surface composition at an elevated temperature, there was no difference between the composition measured at the elevated temperature and that measured at 400 K. For quantitative composition measurements, we used the ratio of the alloy's 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(1 1 1) and Cu(1 1 1) single crystals. The kinetic energies of the Pd $3d_{5/2}$ and Cu $2p_{3/2}$ photoelectrons are 1152 and 555 eV, respectively, corresponding to mean free paths of about 10 Å. Thus, our XPS experiment samples approximately the top seven atomic layers of the sample (>95% of total signal), with about a third of total photoemission signal originating from the topmost layer. We estimate that the reproducibility of our measurements of composition, starting with a newly sputtered and heat-treated sample, is within ±2%.

The low energy ion scattering spectroscopy (LEISS) experiments used 750 eV He^+ ions specularly reflected from the sample surface at an angle ~50° from the sample's surface normal. Low incident ion currents of ~50 nA ($\sim 1.5 \times 10^{13}$ He^+/cm^2 over the course of a single 60 s experiment) were used in order to minimize sputter damage by incident He^+. We observed that significantly higher currents could alter the top layer composition (X_{Cu}^{top}). Also, high He^+ currents incident on the surface over long periods of time changed the composition of the near-surface region (X_{Cu}^{ns}) as measured by XPS. For quantitative estimates of the top layer composition, we compared the LEISS peak areas (Gaussian fits) at $E/E_0 = 0.85$ for Cu and $E/E_0 = 0.91$ for Pd with areas measured for from LEIS spectra of the clean Pd(1 1 1) and Cu(1 1 1) single crystals, using the method outlined by Niehus et al. [23]. We estimate that the reproducibility of our composition measurements by LEISS, starting with a newly sputtered and heat-treated sample, is within ±5%.

We cooled the sample to 120 K for gas adsorption prior to the temperature programmed desorption (TPD) experiments. The chamber pressure was increased to 1×10^{-6} Torr with either H_2 (Matheson) or CO (Matheson) for exposure times of 2 to 10 min to give exposures up to 600 L. The desorption experiment was then conducted by heating the sample at a rate of 4 K/s with the sample located within about 1 mm of the aperture to the mass spectrometer.

3. Results

3.1. XPS analysis

X-ray photoemission has been used to determine the composition of the near-surface region (X_{Cu}^{ns}) of the $Pd_{70}Cu_{30}$ sample. Fig. 1 is an X-ray photoelectron spectrum of the clean sample surface measured at 400 K after annealing at 900 K for 30 min. The Pd $5d_{5/2}$ and Cu $3d_{3/2}$ photoemission features used for quantitative estimates are highlighted. With the exception of a small feature located at ~1240 eV, all features can be assigned to either Pd or Cu.

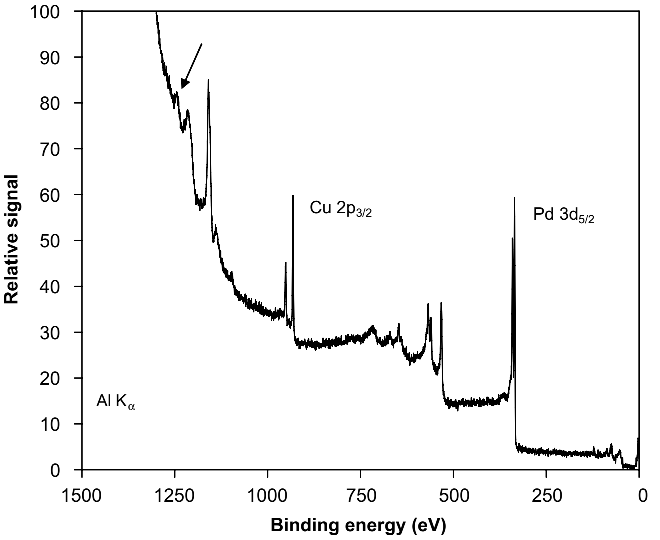

Fig. 1. X-ray photoelectron spectrum of the clean $Pd_{70}Cu_{30}$ alloy after annealing at 900 K for 30 min. The analysis temperature was 400 K. All features, with the exception of the one highlighted by the arrow, can be assigned to either Cu or Pd. The features used for quantitative determination of the composition of the near-surface region are noted.

The composition of the near-surface region (X_{Cu}^{ns}) depends on both anneal temperature and anneal time. After surface preparation by cycles of annealing and Ar^+ sputtering, a final sputter treatment leaves the near-surface region depleted in Cu, with a starting composition of $X_{Cu}^{ns} < 0.22$. Annealing the sputtered sample at 400 K does not significantly change X_{Cu}^{ns}; however, annealing the sputtered sample at temperatures between 600 and 1000 K causes X_{Cu}^{ns} to increase as copper atoms migrate from the bulk to the near-surface region. The near-surface composition is a function of time during annealing of the sputtered sample as illustrated in Fig. 2 for anneal temperatures of 600 and 800 K (solid lines). Steady-state values of X_{Cu}^{ns} are achieved after annealing for ~30 min at these temperatures. These results are consistent with those of Loboda-Cackovic et al. who report depletion of Cu in the near-surface region of a sputtered $Pd_{50}Cu_{50}(1\,1\,0)$ followed by the onset of "Cu segregation" upon annealing at 550 K [12].

The time dependence of the near-surface composition during annealing presumably arises from the diffusion limited transport between the bulk and the surface. Only under conditions of rapid transport is it possible for the alloy's bulk and surface compositions to equilibrate and for the temperature dependence of the surface composition to reflect equilibrium between the bulk and the surface. Therefore, an important consideration is whether or not the steady-state XPS compositions (X_{Cu}^{ns}) observed after 30 min annealing periods are dictated by thermodynamic equilibrium or simply by kinetics. We tested for equilibrium as follows. Recognizing that equilibrium should be approachable from either low X_{Cu}^{ns} (as is generated by

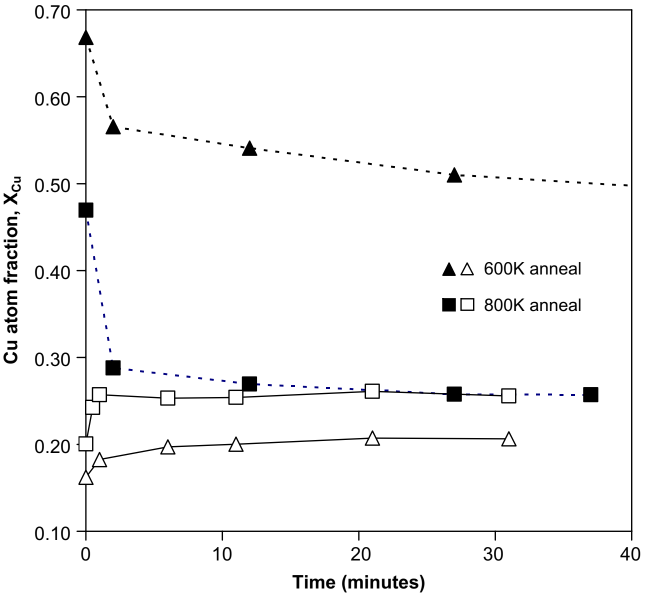

Fig. 2. The composition the XPS-accessible surface region ($X_{\mathrm{Cu}}^{\mathrm{ns}}$) of the $Pd_{70}Cu_{30}$ alloy as a function of anneal time. The solid line/open symbol curves are for surfaces with low starting $X_{\mathrm{Cu}}^{\mathrm{ns}}$ achieved by Ar^+ sputtering at 300 K; steady-state compositions are reached within 30 min. The dotted line/filled symbol curves are for samples with high initial $X_{\mathrm{Cu}}^{\mathrm{ns}}$, achieved by evaporation of incremental copper onto their surfaces. At 800 K, $X_{\mathrm{Cu}}^{\mathrm{ns}}$ approaches the same steady-state from both high and low initial $X_{\mathrm{Cu}}^{\mathrm{ns}}$. At 600 K, the sample with high initial $X_{\mathrm{Cu}}^{\mathrm{ns}}$ does not achieve the sputtered sample's steady-state composition after 2 h (only the first 40 min shown) of annealing.

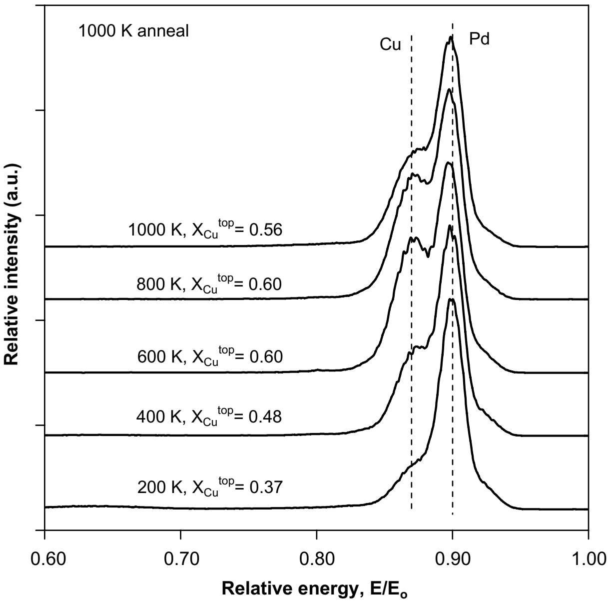

Fig. 3. Low energy ion scattering (LEIS) spectra of the $Pd_{70}Cu_{30}$ alloy annealed at 1000 K as a function of LEISS experiment temperature. The dotted lines show peak locations for Cu and Pd. The Cu concentration in the top layer of the surface ($X_{\mathrm{Cu}}^{\mathrm{top}}$) depends on the temperature of the experiment and goes through a maximum near 700 K.

sputter cleaning of the sample) or high $X_{\mathrm{Cu}}^{\mathrm{ns}}$, we prepared surfaces with $X_{\mathrm{Cu}}^{\mathrm{ns}}$ above the steady-state values by evaporating additional copper onto them, and then measured the time-evolution of their composition during continued annealing. Fig. 2 shows the results of an experiment in which we: (1) annealed the sample at 800 K, (2) cooled it to 400 K for evaporative deposition of Cu onto its surface, and then (3) returned it to 800 K for additional annealing. After Cu deposition, the composition returned to its 800 K steady-state value within about 30 min (dashed line, filled squares). However, when the experiment with the Cu-rich surface was repeated using an annealing temperature of only 600 K (dashed line, filled triangles), the rate of composition change was significantly slower, and the steady-state $X_{\mathrm{Cu}}^{\mathrm{ns}}$ achieved starting with the Cu deficient surface was not recovered after 2 h of annealing at 600 K. These results indicate that the values of $X_{\mathrm{Cu}}^{\mathrm{ns}}$ determined for samples annealed at $\leqslant$600 K are probably kinetically limited and, therefore, do not represent equilibrium surface region compositions. Annealing the sample for 30 min at temperatures $\geqslant$800 K, on the other hand, very likely produces near-surface regions which are in equilibrium with the bulk sample.

3.2. LEISS analysis

Low energy ion scattering spectroscopy (LEISS) was used to determine the composition of the sample's top layer ($X_{\mathrm{Cu}}^{\mathrm{top}}$). Fig. 3 shows a series of LEIS spectra obtained after annealing the sample at 1000 K, but at LEIS temperatures in the range 200–1000 K. Calibration against spectra obtained from pure component, single crystal Pd(1 1 1) and Cu(1 1 1) samples allows us to assign the feature at $E/E_0 = 0.91$ to Pd and the feature at $E/E_0 = 0.85$ to Cu. At temperatures $\leqslant$400 K, low-intensity features tentatively assigned to C and O appear in the spectra at $E/E_0 \sim 0.47$ and 0.67, respectively (not shown in Fig. 3). The top layer compositions determined by LEISS clearly depend on the temperature at which the LEIS spectrum is obtained. In contrast with the results of the XPS experiment that probe the near-surface region, the composition of the top-surface layer reaches steady-state relatively rapidly, within 5 min of achieving sample temperature. Furthermore, the compositions determined for the top layer are reversible in the sense that they are independent of whether that the sample is heated or cooled to the analysis temperature. Therefore, we conclude that our measurements are being made on surfaces at equilibrium with the near-surface region of the sample. LEIS spectra were also collected as a function of temperature for the sample annealed at 800, 600 and 400 K, but are not shown here.

The near-surface ($X_{\mathrm{Cu}}^{\mathrm{ns}}$) and top layer ($X_{\mathrm{Cu}}^{\mathrm{top}}$) compositions of the $Pd_{70}Cu_{30}$ alloy, measured using XPS and LEISS at temperatures between 400 and 1000 K, are summarized in Fig. 4. The values of $X_{\mathrm{Cu}}^{\mathrm{ns}}$ at a given temperature are those measured after annealing at that temperature for 30 min (curve (a)); they do not change during cooling. The values of $X_{\mathrm{Cu}}^{\mathrm{top}}$ have been measured for samples annealed for 30 min at the temperatures indicated in the legend, T_{ann}. The plots of $X_{\mathrm{Cu}}^{\mathrm{top}}$ as functions of temperature show the

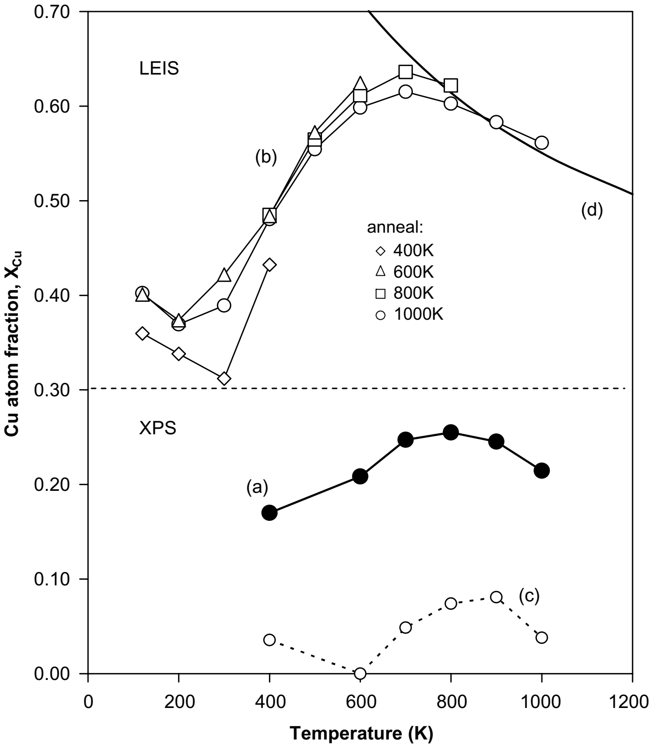

Fig. 4. (a) Composition of the $Pd_{70}Cu_{30}$ alloy's near-surface region (X_{Cu}^{ns}) determined by XPS) as a function of anneal temperature. The sample, sputtered at 300 K, was annealed at temperatures in the range $T_{ann} = 400$–1000 K for 30 min prior to XPS analysis at 400 K. The dotted line shows bulk composition, $X_{Cu}^{bulk} = 0.30$. (b) Compositions of the alloy's topmost atomic layer (X_{Cu}^{top}, determined by LEISS). (c) Composition estimates of the "immediate sub-surface" (~atomic layers 2–7), by algebraically removing the contribution of the top layer from X_{Cu}^{ns}. (d) Top layer compositions from the Langmuir-McLean equation with $\Delta G_s = -8.7$ kJ/mol.

values of X_{Cu}^{top} determined from LEIS spectra obtained at temperatures below T_{ann} (curves (b)). We note that the small increase in the value of X_{Cu}^{top} that occurs as the temperature is reduced below 200 K may be related to preferential adsorption of background CO onto Pd atoms at the lowest temperatures, which could screen the Pd atoms from incident He^+.

3.3. H_2 and CO TPD

Hydrogen and CO adsorption and desorption have been used to probe the nature of the Cu and Pd distribution in the top layer of the alloy surface. Fig. 5 displays H_2 TPD spectra obtained for hydrogen, at saturation coverage, desorbing from the $Pd_{70}Cu_{30}$ alloy surfaces annealed for 30 min at temperatures between 400 and 1000 K. The H_2 TPD spectra obtained after annealing at 400, 600 and 800 K displayed three desorption features, appearing at approximately 175, 235, and 315 K. The 175 K feature has been associated with "sub-surface" absorption of hydrogen in Pd single crystals (Pd-α) [24,25]. The features at 235 and 315 K are probably attributable to recombinative desorption of hydrogen adsorbed on either Cu (Cu-α, -β) or Pd (Pd-β) [24–30]. We note that while the samples annealed at 400, 600, and 800 K all adsorb similar quantities of hydrogen at saturation coverage, the contribution associated with each desorption feature varies with annealing temperature, probably as a result of differences in the top layer and near-surface compositions, surface defect densities and surface topographies. We also note the possibility that adsorbed hydrogen may exert an influence on the surface composition, particularly X_{Cu}^{top}. A detailed interpretation is beyond the scope of this paper, but we note that the possibilities are interesting. For example, it may not be coincidental that after annealing at 800 K, the surface with the highest value of X_{Cu}^{ns}, has the smallest 175 K feature in the hydrogen desorption spectra – which is associated with absorption of H-atoms at subsurface Pd sites.

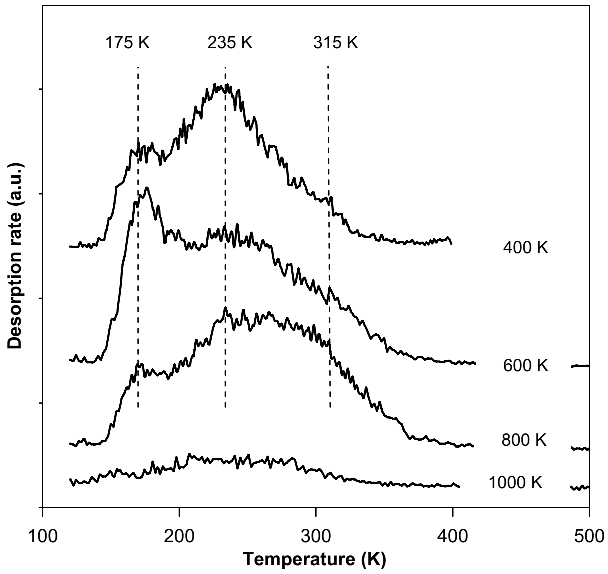

Fig. 5. Hydrogen TPD spectra for the $Pd_{70}Cu_{30}$ alloy for samples initially annealed to temperature in the range 400–1000 K. The surface was exposed to a saturation dose of H_2 at 120 K; heating rate = 4 K/s.

Of primary interest to us is the inability of the surface annealed at 1000 K to adsorb significant amounts of hydrogen. This behavior is typical of copper single crystal surfaces: while the dissociative sticking coefficient for H_2 on Pd is $S_0 \approx 1$, it is extremely low on Cu [24,26,27,30–32]. We note that, when the sample has been annealed at lower temperatures, $T_{ann} \leqslant 800$ K, we cannot rule out the possibility that hydrogen atoms formed by dissociative adsorption on Pd migrate to Cu for recombinative desorption during heating. The 235 and 315 K TPD features may, therefore, have contributions from Cu sites.

CO TPD can also be used to titrate the $Pd_{70}Cu_{30}$ alloy surface and thus be used as a probe of its composition. Fig. 6 shows TPD spectra for saturation coverages of CO adsorbed on sample surfaces annealed at 600 and 1000 K. These anneal temperatures are of particular interest because they display very similar near-surface (X_{Cu}^{ns}) and top layer (X_{Cu}^{top}) compositions as measured by XPS and LEISS (Fig. 4), but very different H_2 TPD spectra (Fig. 5). We

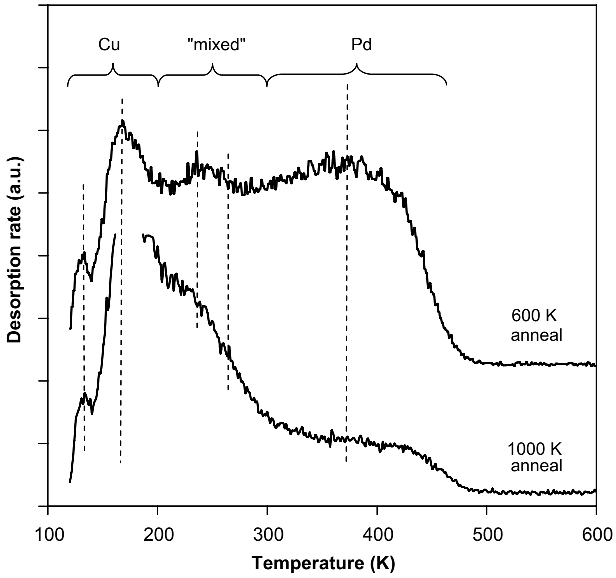

Fig. 6. Carbon monoxide TPD spectra from the $Pd_{70}Cu_{30}$ alloy at after annealing at 600 and 1000 K. Samples were exposed to saturation doses of CO at 120 K; heating rate = 4 K/s. The dotted reference lines are located at 135, 170, 235, 260 and 375 K.

observe four desorption features in the CO TPD spectra, located at 135, 170, 235/260, and 375 K. The features at 135 and 170 K are characteristic of CO desorption from Cu surfaces [33,34]; the high temperature features, in the vicinity of 375 K, are characteristic of CO TPD from highly coordinated sites on Pd surfaces [35,36]. The intermediate temperature features have been assigned to mixed Pd–Cu sites or Pd atoms atop sub-surface Cu [13,34]. It is significant, especially in view of the H_2 TPD results, that the sample annealed at 1000 K displays very little CO desorption from the high temperature state that is characteristic of highly coordinated Pd sites. As was the case for molecular H_2, the surface annealed at 1000 K resembles pure Cu in its interactions with CO.

4. Discussion

During the course of this investigation, two physical probes (XPS and LEISS) have been used to determine the compositions of the near-surface (X_{Cu}^{ns}) and top layer (X_{Cu}^{top}) of a $Pd_{70}Cu_{30}$ alloy annealed to temperatures in the range 400–1000 K. Two chemical probes of surface compositions and chemistries, H_2 and CO adsorption and desorption, have also been employed. In this section, we use our composition measurements and TPD results to describe surface segregation in the $Pd_{70}Cu_{30}$ alloy. We begin with a description of the material's composition depth profile and the temperature dependence of X_{Cu}^{ns} and X_{Cu}^{top}. Then we show that, at 800 K and above, where the bulk, near-surface and top layer are likely to be in equilibrium, the top layer compositions are consistent with those predicted by a simple thermodynamic model. Finally, we illustrate how the annealing of the sputtered sample influences the adsorption of H_2 and CO and we propose a qualitative model of local surface ordering to explain our observations.

There are several important patterns in the XPS and LEISS data set (Fig. 4). While the composition of the near-surface region (X_{Cu}^{ns}, curve (a)) is always below that of the bulk, the top layer composition (X_{Cu}^{top}, curves (b)) is significantly higher than that of the bulk; this difference suggests depletion of Cu in atomic layer(s) immediately below the top. We have estimated the aggregate composition of the "immediate sub-surface" – atomic layers 2–7 – at each anneal temperature by algebraically subtracting the top layer contribution from the value of X_{Cu}^{ns} measured by XPS. The results of the calculation, shown as curve (c) in Fig. 4, illustrate that the immediate sub-surface – perhaps specifically the second atomic layer – is indeed significantly Cu-depleted. A pattern of Cu-rich top-surface and Pd-rich second layer is consistent with the observation [17] and prediction [16] of oscillatory depth profiles in PdCu alloys. Our data do not rule out the possibility that oscillatory composition profiles, consistent with measurements of X_{Cu}^{ns}, continue deeper into the near-surface of the sample. However, because X_{Cu}^{ns} as determined by XPS is an aggregate measure of near-surface composition, we cannot confirm the presence of continued oscillation.

Fig. 4 also illustrates that the top layer compositions measured by LEISS (X_{Cu}^{top}) are independent of the temperature at which the sample has been annealed, T_{ann}, and depend only on the temperature to which it is heated during the LEIS experiment. This result probably reflects the narrow range of composition in the near-surface region (X_{Cu}^{ns}) with which the top layer is in equilibrium. Another significant feature of the data set is that the values of both X_{Cu}^{ns} and X_{Cu}^{top} exhibit maxima with respect to temperature; the location of the maximum is at a slightly lower temperature for the top layer. For a system at thermodynamic equilibrium, such maxima can reflect a change from entropy (order) driven segregation to energy (disorder) driven segregation as the bulk material undergoes an order–disorder (O–D) transition [10]. Because we cannot confirm that the surface region is in equilibrium with the bulk for temperatures < 600 K, our results cannot be interpreted as evidence of a bulk O–D transition. However, we note that at compositions near $X_{Cu}^{bulk} = 0.5$, PdCu exhibits a bulk O–D transition from an ordered BCC phase to a disordered FCC solid solution in the temperature range that we have examined [11,12,19].

Other features of our XPS/LEISS data set are also consistent with those reported by Loboda-Cackovic et al. for a $Pd_{50}Cu_{50}(110)$ single crystal [12]. As the annealing temperature was increased from 400 to 800 K, they observed increasing X_{Cu} in both the near-surface region (measured by Auger electron spectroscopy) and in the top layer (measured by temperature programmed desorption of CO). They also reported Cu enrichment of the top layer relative to the surface region. However, in contrast with our observation that X_{Cu}^{ns} is below the bulk value, they report a Cu-enriched near-surface region (as measured by AES) after annealing their sputtered sample at temperatures between ~550 and 800 K. Part of this discrepancy probably reflects sampling depth differences; we estimate that our XPS experiments sample ~7 atomic layers, Loboda-Cakcovic et al. estimate a ~4 atom layer near-surface region for their AES experiments. Our results are also generally consistent with those Newton and co-workers obtained using a $Pd_{15}Cu_{85}(1\,1\,0)$ single crystal. They report a value of X^{ns}_{Cu} in the XPS-accessible surface region that increased with anneal temperature in the range 300–900 K, and a top layer that was exclusively Cu [17].

At anneal temperatures $\geqslant 800$ K, where the bulk, near-surface region, and top layer are likely to be in equilibrium, we can analyze the top layer compositions measured by LEISS to estimate a thermodynamic driving force for Cu segregation to the top layer. For the case of a binary, regular solution (random distribution of atoms, with no assumptions about heat of mixing), the Gibbs adsorption isotherm can be expressed as [10,37–40]:

$$\frac{X^{top}_{Cu}}{X^{top}_{Pd}} = \frac{X^{bulk}_{Cu}}{X^{bulk}_{Pd}} \cdot \exp\left(\frac{-\Delta G_s}{RT}\right)$$

In this expression, known as the Langmuir-McLean equation [10,40], ΔG_s is the Gibbs free energy of segregation. It represents the free energy change when Cu (solute) atoms from the bulk replace Pd (solvent) atoms at the surface [10,37]. Application of the equation to the top-surface compositions measured at $\geqslant 800$ K for the sample annealed at 1000 K (Fig. 4) provides an estimate of $\Delta G_s = -8.7$ kJ/mol. For comparison with the measured values, Fig. 4 includes a plot of surface compositions calculated from Langmuir-McLean with $\Delta G_s = -8.7$ kJ/mol (curve (d)).

The estimate of $\Delta G_s = -8.7$ kJ/mol derived from segregation measurements compares favorably with predictions based solely on the surface free energy (surface tension) difference between the pure components. For this case, $\Delta G_s = N_A(\gamma_{Cu} - \gamma_{Pd})/a$ where, N_A is Avogadro's Number, γ_{Pd} and γ_{Cu} are the pure component surface tensions, 2.05 and 1.83 J/m^2, respectively [41,42], and a is the surface atom density, 1.6×10^{19} $atoms/m^2$, an average for Pd(1 1 1) and Cu(1 1 1). The result, $\Delta G_s = -8.3$ kJ/mol, is comparable to the experimental value, suggesting that the surface tension difference could be the main driver of segregation in this system.

Our TPD results bring an additional dimension to our understanding of the details of segregation in the $Pd_{70}Cu_{30}$ alloy. The relative magnitudes of the CO and H_2 TPD desorption features change significantly as a function of anneal temperature. This is an interesting observation because, over the range of temperatures encountered in the TPD experiment—120 to 500 K—the top layer compositions are the same for all anneal temperatures except 400 K (Fig. 4). Perhaps the most compelling comparison is between the TPD spectra obtained from the sample annealed at 600 K and at 1000 K. When annealed at 600 K, the sample surface readily adsorbs both hydrogen and carbon monoxide. However, upon annealing at 1000 K, it adsorbs no hydrogen and very little CO in the high temperature state—behaviors that are characteristic of a pure Cu surface. These differences exist despite the fact that both the near-surface compositions (X^{ns}_{Cu}) and top layer compositions (X^{top}_{Cu}) at those anneal temperatures are almost identical (Fig. 4). We note that surface defects, which may exist at lower densities after annealing at higher temperatures, could contribute to the TPD differences at low desorption temperatures. However, the high temperature TPD features are characteristic of desorption from smooth surfaces, and differences in this region of the spectra very likely reflect only differences in the local arrangement of the atoms in the top layer of the sample surface.

Fig. 7 shows schematic models of the surface that may explain the differences in the TPD spectra obtained from the samples annealed at 600 and 1000 K. The sputtered sample may display short range order [12], which could include lateral segregation of Pd and Cu components into islands. Annealing for 30 min at 600 K may not disturb this order, either because thermodynamic equilibrium has not been achieved or because the equilibrium state below the system's order–disorder (O–D) transition temperature is, in fact, ordered. In either case, persistence of the islands at 600 K (Fig. 7) allows them to display local H_2 and CO surface chemistries (Figs. 5 and 6) that are characteristic of pure Pd and Cu. Annealing at 1000 K, above the O–D transition, may, on the other hand, disrupt the local order to form a randomly distributed top layer; this scenario is consistent with Loboda-Cackovic's report of the onset of surface disordering at ~700 K in $Pd_{50}Cu_{50}(1\,1\,0)$ [43,44]. Such a disordered top layer possesses neither the "Pd ensembles" required for dissociative adsorption of H_2 [45,46] nor the highly coordinated Pd sites associated with the high temperature CO desorption features [35,47].

As noted earlier, dissociative H_2 adsorption is the first step in hydrogen transport through a dense metal hydrogen purification membrane. Given our observation that, when annealed at 1000 K, the alloy does not adsorb a significant amount of hydrogen, we might expect that $Pd_{70}Cu_{30}$ would be a poor choice for hydrogen purification at 1000 K. Permeability tests of the $Pd_{70}Cu_{30}$ membranes demonstrate that this is not the case; both in a clean environment [6] and in the

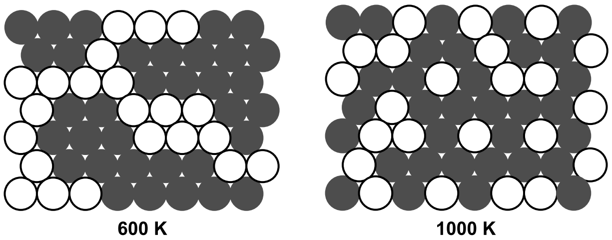

Fig. 7. Qualitative model of the distribution of Cu and Pd in the top layer of a PdCu alloy annealed at 600 and 1000 K. Although the compositions of the two surfaces are identical, the distribution of atoms in the top layer differs and gives rise to differences in their surface chemistry.

presence of an H_2S poison [6], the alloy displays significant hydrogen permeance. The most likely reason for this apparent discrepancy is that H_2 dissociation could be thermally activated at 1000 K. It is also possible that segregation patterns we report here are not the same as those encountered during the permeability measurement. For example, in a follow-up paper we will report our findings that adsorbed sulfur (introduced as H_2S) significantly affects segregation, exposing a top layer that contains no copper.

5. Conclusions

The XPS-accessible near-surface region of a polycrystalline $Pd_{70}Cu_{30}$ alloy becomes enriched in palladium during surface preparation by cycles of high temperature annealing and Ar^+ sputtering at 300 K. Annealing of the sputtered surface to temperatures between 600 and 1000 K causes Cu atoms to migrate from the bulk to the surface region, but the copper concentrations in the near-surface region (X^{ns}_{Cu}) remain below that of the bulk. In contrast, top layer compositions (X^{top}_{Cu}) measured by LEISS, are copper rich relative to the bulk. For anneal temperatures at or above 600 K, the top layer compositions do not depend on the annealing history, but do depend on the temperature at which the LEISS experiment is performed. For anneal temperatures $\geqslant 800$ K, where the bulk, near-surface, and top layer are likely in thermodynamic equilibrium, the temperature dependence of top layer composition can be described by a simple Langmuir-McLean isotherm. The measured free energy of segregation compares well with that expected for a case in which pure the component surface tension difference is the primary driver of segregation. Despite nearly identical surface region and top layer compositions after annealing at 600 K and 1000 K, the CO and H_2 TPD spectra are very different – the surface annealed at 1000 K does not display the desorption features associated with highly coordinated Pd sites that are present the spectra obtained from the surface annealed at 600 K. The TPD results may be explained by a change in the local arrangement of atoms in the top layer in which Pd and Cu "islands" present at 600 K become randomly distributed Pd and Cu atoms at 1000 K.

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