Surface Segregation in a PdCu Alloy Hydrogen Separation Membrane

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Introduction

Separation of hydrogen from mixed gas streams is an important step for hydrogen generation technologies, including hydrocarbon reforming and coal/biomass gasification. Dense palladium-based membranes have received significant attention for this application because of palladium's ability to dissociatively adsorb molecular hydrogen at its surface for subsequent transport of hydrogen atoms through its bulk. Alloying palladium with minor components, like copper, has been shown to improve both the membrane's structural characteristics and resistance to poisoning of its catalytic surface [1].

Surface segregation—a composition difference between the bulk material and its surface—is common in alloys and can affect important surface processes. Rational design of alloy membranes requires that surface segregation be understood, and possibly controlled. In this work, we examine surface segregation in a polycrystalline $Pd_{70}Cu_{30}$ hydrogen separation membrane as a function of thermal treatment and adsorption of hydrogen sulfide.

Materials and Methods

We purchased the $Pd_{70}Cu_{30}$ alloy from ACI and cold-rolled it to 1mm thickness. We performed all experiments in a stainless steel ultra-high vacuum chamber with a base pressure of 1 x 10^{-10} torr. The chamber is equipped with a monochromated X-ray source for X-ray Photoelectron Spectroscopy (XPS), an ion gun for Low Energy Ion (He+) Scattering (LEIS) and a mass spectrometer for Temperature Programmed Desorption (TPD).

Prior to experimentation, we prepared the surface of the sample by cycles of high temperature (1000K) annealing and room temperature Ar+ sputtering. After the final sputter, we annealed the sample for 30 minutes (to steady state XPS composition) at 400, 600, 800, or 1000K. For the sample annealed at each temperature, we performed a series of LEIS experiments at temperatures equal to or below that of the corresponding anneal.

Results and Discussion

The lower portion of Figure 1 shows the composition of the XPS-accessible region of the sample as a function of anneal temperature. Composition in this region—about 10 atomic layers into the sample—exhibits a maximum in copper content at 800K, but is always palladium rich relative to the bulk. The upper portion of Figure 1 shows LEIS-determined top-layer compositions as functions of anneal temperature (different curves) and temperature of the LEIS experiment (horizontal axis). Top layer composition does not strongly depend on anneal temperature (curves for 600, 800, and 100K anneals are coincident). In contrast to the XPS-accessible region, the top layer is always copper rich relative to the bulk. But like the XPS-accessible region, the top-layer composition exhibits a maximum with respect to temperature. Such a maximum is consistent with an order-disorder (O-D) transition [2]. At temperatures above the O-D transition, top-layer compositions are consistent with those predicted by a simple (ideal solution) thermodynamic model [2].

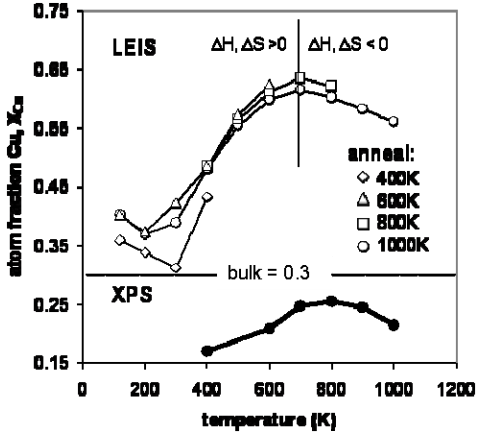

Figure 1. LEIS (upper) and XPS (lower) compositions of the alloy sample as functions of temperature. For quantitative composition estimates, both experiments were calibrated against Pd(111) and Cu(111) standards. Horizontal line shows the bulk composition

Despite very similar XPS and LEIS compositions, when annealed at 600 and 1000K, the sample exhibits very different CO and H_2 TPD spectra: the 600K-annealed sample displays features associated with both pure Pd and pure Cu, while the 1000K-annealed sample displays features of Cu-only. We attribute this observation to differences in local ordering within the top layer—separate Pd and Cu regions at 600K (order) vs. random distribution of Pd and Cu (disorder) at 1000K.

Adsorption of sulfur as hydrogen sulfide increases the palladium enrichment of the XPS-accessible surface region and results in a "palladium-only" top layer, illustrating how the presence of an adatom can significantly affect segregation patterns.

Significance

Top layer compositions can differ significantly from surface-region compositions, which in turn can be very different from the bulk. Segregation patterns—and surface activities that depend on them—change with ambient temperature, heat-treatment history and presence of adsorbed species. Our results provide a basis for understanding, and eventually controlling, segregation for rational design and implementation of alloy separation membranes.

References

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2. Polak, M., L. Rubinovich, *Colloids and Surfaces A*, 2002. **208**: p. 211-218.