**Core-level shifts in Cu-Pd alloys as a function of bulk composition and structure**

The properties of metallic alloys typically depend on alloy composition and often have regions of composition space over which they are superior to those of the pure elemental components. Finding these regions and understanding the relationship between alloy properties and composition is a core problem of metallurgy and, more generally, the science of multicomponent materials. Very often, properties of interest are strong functions of alloy phase, in which case the properties can vary discontinuously across phase boundaries in composition space. This work demonstrates a method for experimental observation of phase boundaries in alloys based on the measurement of core level shifts (CLS) in x-ray photoemission spectroscopy (XPS) and for modelling CLS’s using Density Functional Theory (DFT). It also demonstrates a high throughput method for mapping of CLS’s with almost continuous composition resolution across large and continuous regions of alloy composition space. The ability to use XPS to identify phases makes the approach particularly useful for study of phases present in the near surface regions (~1-2 nm) of alloys, in thin films, and in nanoparticulate morphologies; materials whose atomistic structures may not be amenable to study by x-ray diffraction or other structural tools.

Cu*x*Pd1-*x* alloys have been studied extensively for use as hydrogen purification membranes.[1-7](#_ENREF_1) Pd and many of its alloys are used to separate hydrogen from gas streams because their surfaces readily dissociate H2 and because H atoms have high permeance through the Pd alloy lattice. Alloying Pd with elements such as Cu increases the mechanical strength of the membrane and also imparts tolerance to the presence of sulfur containing compounds that would otherwise poison the membrane surface. Cu*x*Pd1-*x* alloy properties such as mechanical strength, H2 dissociation kinetics, H-atom permeance, and sulfur tolerance depend on the alloy composition, *x*, and on alloy phase.[1](#_ENREF_1),[3](#_ENREF_3),[7-9](#_ENREF_7) In this regard, Cu*x*Pd1-*x* has an interesting phase diagram. Although pure Cu and Pd both have face-centered-cubic (FCC) bulk structures, Cu*x*Pd1-*x* forms a B2 phase (BCC-like, CsCl structure) at *x* ≈ 0.4 and T < 870 K. This B2 region expands to 0.35 < *x* < 0.45 at T = 700 K.[ref] Furthermore, some of the Cu*x*Pd1-*x* alloy properties critical to their performance in hydrogen separation depend on phase. For example, the solubility of H-atoms in the B2 phase is roughly 5× lower than in the FCC phase.[7](#_ENREF_7) However, the net permeance of H-atoms is almost 10× higher in the open lattice of the B2 phase than in the close-packed FCC lattice.[10](#_ENREF_10) Thus, stabilizing the B2 phase to temperatures >870 K would greatly improve Cu*x*Pd1-*x* membrane performance under desired operating conditions. The kinetics of H2 dissociation are much faster on the FCC phase than on the B2 phase.[8](#_ENREF_8) The work described herein provides a means of using high throughput XPS measurements of Cu 2p3/2 CLS’s to map the composition region of the B2 phase as a function of temperature for Cu*x*Pd1-*x* or ternary Cu*x*X*y*Pd1-*x-y* alloys.

**2.1. Experimental**

The Cu*x*Pd1-*x* alloy samples used for XPS measurements were thin (~100 nm) films deposited on Mo substrates. The key experimental innovation used in this work is the use of composition spread alloy films (CSAFs) deposited such that the films have composition gradients lateral to their surfaces. These are high throughput materials libraries with a continuous distribution of local compositions across a lateral dimension of ~1 cm. The CSAFs have been deposited under ultra-high vacuum conditions using either an offset filament deposition tool or a rotating shadow mask deposition tool; both yield the same types of CSAFs and the same observations of CLS’s reported in this work.[11](#_ENREF_11),[12](#_ENREF_12) The CSAFs have been deposited at room temperature over periods of 6-8 hrs and then annealed to 800 K for 1 hr to induce crystallization.

Spatially resolved XPS analysis of the Cu*x*Pd1-*x* CSAF was conducted using a ThermoFisher ThetaProbe and yielded XP spectra from Cu*x*Pd1-*x* alloys films spanning the entire composition space, *x* = 0 → 1. XP spectra were obtained using a 200 μm diameter, monochromated Al Kα x-ray spot and by moving the CSAF beneath the spot to access regions of different composition. At each point, or alloy composition, XP spectra were obtained for the Cu 2p3/2 and Pd 3d5/2 lines taking 20 sec for each element and using a 40 eV analyzer pass energy.

At each analysis composition, the films were sputtered for 6 minutes using a He+ beam with an oval profile of 500 × 700 μm2, a current of 4.4 μA, and a beam energy of 1 keV. This was sufficient to remove any residual O or C contamination from the surface of the film. Following sputtering, the CSAF was annealed at temperatures of 400, 500, 600, 700, and 800 K to recrystallize the near surface region damaged by He+ sputtering. XPS did reveal a small amount of preferential sputtering of Cu from the near surface region. After sputtering at 300 K, this resulted in <5% change in local alloy composition relative to the composition generated by annealing at 800 K. The alloy composition was restored to the value observed at 800 K by annealing to 600 K. This type of behavior is consistent with prior observations of segregation in Pd70Cu30 alloys.[5](#_ENREF_5)

**3. Results**

The discontinuous CLS at compositions near those of the B2 phase suggests that the origin of the discontinuity is associated with the transition from the close-packed FCC lattice to the more open BCC lattice of the B2 phase. Additional evidence for this comes from XPS study of the CSAF following He+ ion sputtering. Figure 3.2 shows the Cu 2p3/2 binding energy versus Cu*x*Pd1-*x* composition as measured on CSAF deposited using the rotating shadow mask CSAF deposition tool.[11](#_ENREF_11) This CSAF spans the entire binary alloy composition space. The CSAF preparation includes annealing at 800 K for 1 hrs prior to removal from the deposition chamber. This as-prepared CSAF exhibits the Cu 2p3/2 CLS behavior (not shown) associated with the B2 phase (Figure 3). Sputtering of the CSAF with He+ at 1 keV causes sufficient damage to the near surface region that the FCC-B2-FCC transition is no longer observed in the CLS measurements (Figure 3.2, solid black squares). However, after annealing the CSAF in vacuum at 800 K for 1 hr the CLS discontinuity (solid red circles) associated with the B2 phase reappears. In fact, the B2 phase appears to be fully formed after annealing at only 600 K for 1 hr.



**Figure 3.2.**  Cu 2p3/2 core level binding energy versus Cu*x*Pd1-*x* composition. The Cu 2p3/2 binding energies measured after He+ ion sputtering at 1 keV for 6 minutes (solid black squares) show a clear suppression of the CLS associated with the B2 phase. This B2-related CLS reappears after annealing at 800 K for 60 minutes (solid red circles).

**References**

(1) Kulprathipanja, A.; Alptekin, G. O.; Falconer, J. L.; Way, J. D. *Journal Of Membrane Science* **2005**, *254*, 49.

(2) Morreale, B. D.; Howard, B. H.; Iyoha, O.; Enick, R. M.; Ling, C.; Sholl, D. S. *Industrial & Engineering Chemistry Research* **2007**, *46*, 6313.

(3) O'Brien, C. P.; Howard, B. H.; Miller, J. B.; Morreale, B. D.; Gellman, A. J. *Journal of Membrane Science* **2010**, *349*, 380.

(4) Paglieri, S. N.; Way, J. D. *Separation And Purification Methods* **2002**, *31*, 1.

(5) Miller, J. B.; Matranga, C.; Gellman, A. J. *Surface Science* **2008**, *602*, 375.

(6) Peters, T. A.; Kaleta, T.; Stange, M.; Bredesen, R. *Journal Of Membrane Science* **2011**, *383*, 124.

(7) Martin, M. H.; Galipaud, J.; Tranchot, A.; Roue, L.; Guay, D. *Electrochimica Acta* **2013**, *90*, 615.

(8) O'Brien, C. P.; Miller, J. B.; Morreale, B. D.; Gellman, A. J. *J Phys Chem C* **2011**, *115*, 24221.

(9) O'Brien, C. P.; Miller, J. B.; Morreale, B. D.; Gellman, A. J. *J Phys Chem C* **2012**, *116*, 17657.

(10) Kamakoti, P.; Morreale, B. D.; Ciocco, M. V.; Howard, B. H.; Killmeyer, R. P.; Cugini, A. V.; Sholl, D. S. *Science* **2005**, *307*, 569.

(11) Fleutot, B.; Miller, J. B.; Gellman, A. J. *Journal of Vacuum Science & Technology A* **2012**, *30*.

(12) Priyadarshini, D.; Kondratyuk, P.; Miller, J. B.; Gellman, A. J. *Journal of Vacuum Science & Technology A* **2012**, *30*.