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## LETTER TO THE EDITOR

## Surface-induced phase separation in Pd–Ag alloy: the case opposite to surface alloying

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Online at [stacks.iop.org/JPhysCM/15/L415](http://stacks.iop.org/JPhysCM/15/L415)**Abstract**

Since Pd–Ag alloys constitute a well known prototype binary alloy system, phase separation at the surface was not expected. However, we have shown direct evidence of surface-induced phase separation in Pd–Ag alloys using photoemission spectroscopy. This phenomenon is just the opposite of surface alloying between two miscible elements. The miscibility gap in this alloy near the surface is clearly observed in our core level spectra. The characteristics of this surface-induced phase separation have been probed over various composition ranges using x-ray photoelectron spectroscopy.

Understanding an alloy system requires detailed information on its energetics and local atomic and electronic structure. This becomes more complicated when it has broken translational symmetry, e.g. when there is a surface present. For example, surface alloying in a two-miscible-element bimetallic system has recently attracted a great of attention, since observation of atomic scale alloying has become possible with the scanning tunnelling microscope [1]. This is potentially quite important for the exact evaluation of interfaces, since the interface determines the overall characteristics of thin layered systems, especially those of magnetic multilayers which show giant magnetoresistivity [2]. Our observation here is of a phenomenon which is opposite to this surface alloying. In this letter, we will give direct evidence of phase separation in a Pd–Ag alloy just near the surface region. Our direct evidence comes from a high-resolution study of core level spectra from x-ray photoelectron spectroscopy. This phenomenon should be distinguished from surface segregation, which results in a major distribution of one component at the surface over the other.

The Pd–Ag system is well known as a binary alloy system with no miscibility gap over the entire composition range; i.e. it forms a disordered metallic solid solution below the melting

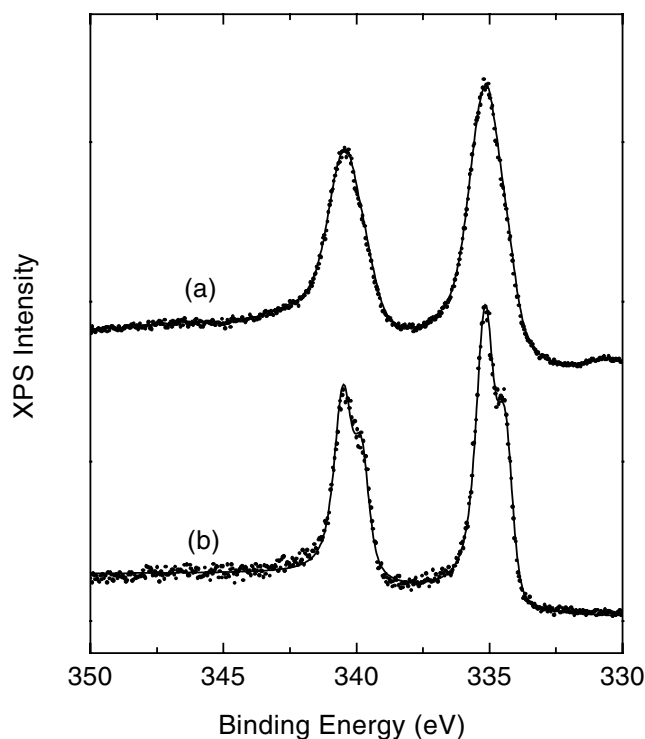
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temperature [3]. So this system has long been frequently used as a reference material in the study of the electronic structure of alloys in general approaches [4–9]. Previous theoretical and experimental reports on Pd–Ag alloys have mostly focused on the bulk properties, although some experimental techniques are surface sensitive. The electronic structure associated with a particular local configuration of atoms in the substitutionally disordered alloy  $\text{Pd}_{1-x}\text{Ag}_x$  has been reported [10]. It is based on methods for treating a cluster or impurity atoms embedded in a translationally invariant medium. For various configurations of Pd and Ag, the average site energy (band energy/site) in the  $\text{Pd}_{0.5}\text{Ag}_{0.5}$  alloy increases as the number of like near neighbours increases. This means that unlike near neighbours are energetically favoured over like near neighbours in the bulk alloys. The heat of solution of the disordered phase and several stoichiometric compounds have been calculated using an analytic embedded atom method (EAM) with no adjustable parameter for Pd–Ag [11–14]. In these calculations, alloys involving Pd do not yield good agreement with experiments. So far there have been no notable theoretical reports on the phenomena at the surface of the Pd–Ag alloys.

All of our samples of Pd–Ag alloys were made by the arc-melting method. After they had been melted, these samples were homogenized by annealing at 850 °C for 40 h after vacuum sealing. The base pressure of the UHV system was maintained at less than  $7 \times 10^{-11}$  Torr. The sample surface was cleaned by minimum bombardment with low-energy Ar ions (500 eV) to remove the oxygen and carbon contamination. In this way, we were able to produce oxygen- and carbon-free surfaces. The spectral area of each element in the core level spectrum, with consideration of the inelastic mean free path, is almost proportional to the composition ratio under such cleaning conditions [15]. This means that there is little preferential sputtering or surface segregation (or enrichment) during the sample cleaning by this procedure. X-ray photoelectron spectra were taken with the ESCALAB220 system equipped with a hemispherical analyser in the fixed analyser transmission mode. We used a monochromatized Al  $K\alpha$  line as our photon source. The pass energy was 8 eV for the core level spectra of Pd  $3d_{5/2}$  and Ag  $3d_{5/2}$ , where the best maximum counts with the best resolution can be obtained. The overall resolution of our system was 400 meV.

We show the x-ray photoelectron spectrum of the Pd 3d core levels obtained using a non-monochromatized Al anode source in figure 1(a) and the spectrum obtained using a monochromatized source in figure 1(b). Without the monochromatized source, the deconvolution of the Pd 3d core level into two components is quite unlikely. Instead, an asymmetric single peak is probable since we cannot expect any other component of the peak in our spectrum according to previous reports. We also checked the variation of the lattice constant in this alloy using x-ray diffraction. Obviously the lattice constant of these alloys follows Vegard's law. This shows that our samples are the same as others as far as the bulk properties are concerned. Because the intensity ratio of the separated core levels varied with the composition, as will be shown later, the core level shift obtained with the non-monochromatized source may lead to misunderstanding of the chemical shift obtained with the non-monochromatized source, which may in turn lead to misunderstanding of the chemical state of the sample [16–18]. An earlier report on the core level of Pd showed a shift towards higher binding energies [19]. This could be due to hydrogen contamination [20, 21] especially in thin-film-type samples. The most recent report showed the same tendency of the core level shift as our observation [22].

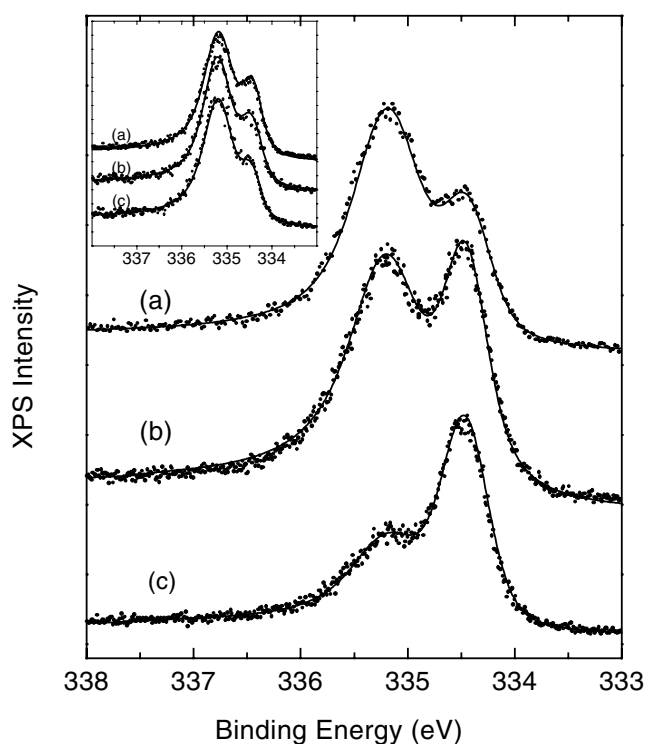
The x-ray photoelectron spectra of the Pd  $3d_{5/2}$  core level for different compositions of Pd in  $\text{Pd}_{1-x}\text{Ag}_x$  (the  $x$ -values are 0.25, 0.5 and 0.75) are shown in figure 2. As the amount of Pd increases, the intensity of the higher-binding-energy peak (peak A) of the Pd  $3d_{5/2}$  core level increases. Also, the intensity of the lower-binding-energy peak (peak B) of Pd  $3d_{5/2}$  is proportional to the concentration of Ag. We have fitted these peaks with the Doniach–Šunjic



**Figure 1.** X-ray photoelectron spectra of the Pd 3d core levels in  $\text{Pd}_{1-x}\text{Ag}_x$  obtained with (a) non-monochromatized and (b) monochromatized x-ray sources.

function and added a Gaussian form to account for instrumental broadening. The binding energies of the two peaks are 335.2 eV (peak A) and 334.4 eV (peak B). The position of peak A is almost invariant with the composition ratio of the alloys and the change in the position of peak B is within 0.1 eV. The full width at half-maximum of peak A is broader than that of peak B, which results from the difference in surrounding valence band configuration of the Pd site. The position of peak A corresponds to the binding energy of clean Pd  $3d_{5/2}$ . The intensity ratio between peak A and peak B increases monotonically as the concentration of Pd increases in Pd–Ag alloys. The inset of figure 2 shows the dependence of the take-off angle of Pd  $3d_{5/2}$  core electrons in  $\text{Pd}_{0.75}\text{Ag}_{0.25}$ . The angles are (a)  $0^\circ$  (b)  $30^\circ$  and (c)  $60^\circ$  from the surface normal. The relative intensity of the peak increases slightly as the take-off angle increases. However, the intensity ratio between peak A and peak B never follows the cosine law. If this additional peak is due to the surface segregation of Pd, a large angle dependence of the segregated element should follow, which is not found in this system. To summarize the results so far, two conclusions can be drawn. First, there are two different chemical environments for Pd. Second, one of them (leading to peak A) is more related to Pd bulk characteristics while another (leading to peak B) is related to Pd in Ag surroundings.

To give a deeper understanding of the spectrum of this alloy system, we have shown the model picture of the surface of the alloy in figure 3, based on the analysis of our spectrum. There are actually three possible situations. The first one is the scraped surface of the sample; the composition of this surface should be the same as that of the bulk. The second one is the surface of the so-called ‘phase-separated case’; the overall intensity ratio of core levels between the two compositions is the same as that for the first picture, but there are two regions

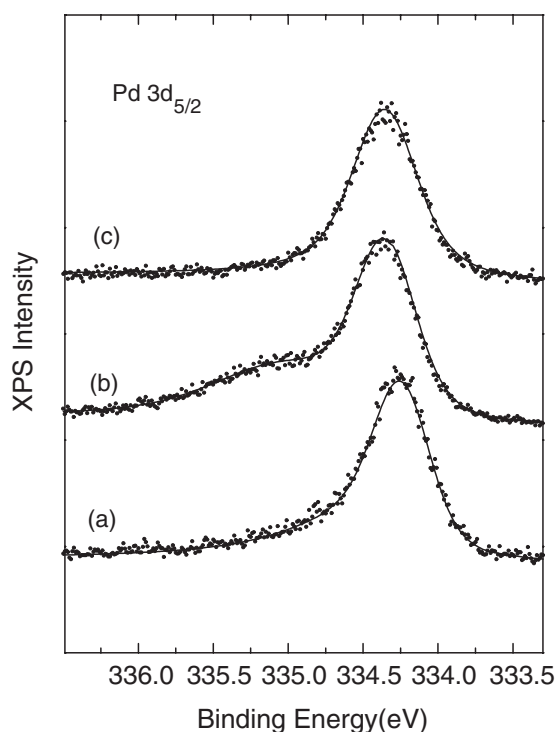


**Figure 2.** X-ray photoelectron spectra of the Pd  $3d_{5/2}$  core level in (a)  $\text{Pd}_{0.75}\text{Ag}_{0.25}$ , (b)  $\text{Pd}_{0.5}\text{Ag}_{0.5}$  and (c)  $\text{Pd}_{0.25}\text{Ag}_{0.75}$ . The inset reveals the angle dependence of the core level spectra of Pd  $3d_{5/2}$  in  $\text{Pd}_{0.75}\text{Ag}_{0.25}$ . The angles are (a)  $0^\circ$ , (b)  $30^\circ$  and (c)  $60^\circ$  from the surface normal.

where pure silver and palladium have been phase separated at the surface. The third one is alloy termination with segregated Ag on top of it.

To get a clear understanding of the origin of this state, we scraped the sample, and followed this treatment by high-energy (2 keV) Ar ion irradiation and annealing. The spectra of the Pd  $3d_{5/2}$  core levels in each case are shown in figure 3. Right after the scraping, the higher-binding-energy state disappears and the lower-binding-energy state shifts towards the Fermi level (figure 3(a)). This means that right after the scraping, the surface state is much the same as the bulk alloy state. Figure 3(b) shows the Pd  $3d_{5/2}$  core level spectrum taken after 2 kV Ar ion irradiation of the scraped sample surface. A new broad peak appears on the higher-binding-energy side. The position and the FWHM of the new peak are 335.2 and 1.1 eV, respectively, identical to the values for peak A in figure 2. This result clearly eliminates the possibility of hydrogen or oxygen contamination. Also, if this higher-binding-energy state, which is located at the binding energy of bulk Pd, was due to surface segregation, this peak should disappear upon sputtering<sup>4</sup>. The Pd  $3d_{5/2}$  core level spectrum of the sample annealed at  $600^\circ\text{C}$  inside the measurement chamber is shown in figure 3(c). In this spectrum, only a single peak (B) showed up. Its position and FWHM are 334.4 and 0.55 eV, respectively. This shows that peak A disappeared upon annealing. However, the position of peak B is not the same as the peak for the scraped sample. This is due to the surface segregation of Ag at high temperature. One

<sup>4</sup> There was slight surface segregation of this alloy and it was Ag which segregated to the top. The effect of this segregation on the intensity of the Pd core level was less than 10% before the low-energy sputtering. After the low-energy sputtering, this segregated Ag had ceased.

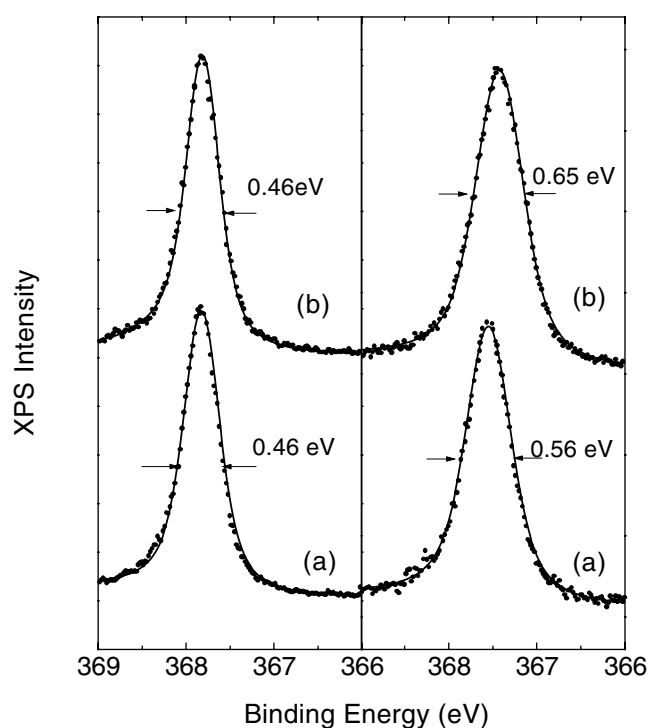


**Figure 3.** X-ray photoelectron spectra of the Pd  $3d_{5/2}$  core level in  $\text{Pd}_{0.25}\text{Ag}_{0.75}$  which was (a) scraped, (b) irradiated with Ar ions after being annealed and (c) annealed at  $600^\circ\text{C}$ .

might argue that peak A is due to hydrogen contamination. Earlier reports on the H/Pd system showed a higher-binding-energy state (+0.15 eV) compared with that of pure Pd [20, 23]. But the peak due to hydrogen contamination cannot be generated with high-energy Ar ions, as shown in figure 3(b). Interestingly, this higher-binding-energy state showed up after several days in the UHV chamber, starting with an annealed or scraped sample. One can eliminate the ion beam effect as the possible explanation of this phenomenon: the phenomenon that we observed does not originate from an ion-beam-induced effect, nor is it due to a contaminant at the surface. Surface segregation or preferential sputtering cannot explain all these results.

Among all the possible explanations, phase separation induced by the surface is the only solution that can explain all the experimental results clearly. To give a clear explanation, an overall picture of the surface of this Ag–Pd alloy should be proposed. Inside the bulk system, there is no deviation from the bulk alloy, as we expected. However, at least within the probing depth of photoemitted electrons, Ag and Pd are separated to form small clusters. These clusters are big enough to show bulk properties and small enough that the surface contributions of these clusters are quite comparable to the bulk contributions. For example, Pd atoms near the centre of a Pd cluster reveal bulk characteristics, but Pd atoms adjacent to Ag clusters show the behaviour of a Ag–Pd alloy. This picture can clearly explain the bimodal behaviour of this core level spectrum<sup>5</sup>. If this cluster size is bigger than 3–5 atomic units on one side, we could expect a kind of 50–50% alloy at the interface. The time constant for this phase separation is

<sup>5</sup> One can expect in principle 12 different Pd states according to the number of Ag neighbours in the fcc structure. However, one must bear in mind that the lower-binding-energy state of Pd 3d comes from the interface of the two separated clusters.



**Figure 4.** X-ray photoelectron spectra of the Ag  $3d_{5/2}$  core level in  $\text{Pd}_{1-x}\text{Ag}_x$  which was (a) annealed at  $600^\circ\text{C}$  and (b) irradiated with Ar ions after annealing.

relatively large. Bombarding this surface with high-energy (2 keV) ion beams can accelerate this phase separation. In solids, collisional processes result in the generation of point defects within the volume of the collision cascade itself. The lifetimes of these defects are not long enough for them to diffuse much beyond the collision cascade, so they cannot extend far below the range of irradiated ions. Also, more vacancies near the surface generated by the ion irradiation will speed up this separation [24]. The kinetic energy released by the ions can be used to overcome the diffusion barrier, assuming the same defect density. This irradiation-assisted transformation was proved to occur in other important binary systems also [25]. The next question is that of the range of compositions in this alloy for which this phase separation will occur.

Further proof of phase separation for a range of compositions can be found in the spectrum of Ag shown in figure 4. We cannot clearly resolve two different species of Ag, since the separation is very small. On the left of figure 4 are the x-ray photoelectron spectra of the Ag  $3d_{5/2}$  core level of  $\text{Pd}_{0.05}\text{Ag}_{0.95}$  and on the right are those of  $\text{Pd}_{0.5}\text{Ag}_{0.5}$ . In each part, (a) was obtained after sample annealing and (b) was obtained after Ar ion irradiation. In the  $\text{Pd}_{0.5}\text{Ag}_{0.5}$  case, the FWHM of the Ag  $3d_{5/2}$  core level is increased by 16% upon Ar ion irradiation, from 0.56 to 0.65 eV. This is due to two different species of Ag being formed after the Ar ion irradiation. But in  $\text{Pd}_{0.05}\text{Ag}_{0.95}$ , the FWHM is 0.46 eV, which is not altered upon Ar ion irradiation. In this case, there was no higher-binding-energy state in the core level spectrum of Pd  $3d_{5/2}$ . This is related to the boundary of this phase separation in the phase diagram. As we have shown in figure 2, peak B has constant intensity regardless of the bulk concentration. This intensity corresponds to approximately 18% of the Pd concentration. Below this value,

peak A for the Pd 3d<sub>5/2</sub> core level does not appear. We have tested this with 5 and 10% Pd concentrations. These samples show only the lower-binding-energy state (peak B).

The microscopic origin of this phase separation at the surface is not clear at present. However, we believe that the phase separation in the alloy surface results from the different electronic structure of the alloy surface as compared with that of the bulk. It has been shown that the d bandwidth of Ag is strongly dependent on the distance of the neighbouring Ag atom [26]. This is also the case for Pd [27]. Upon alloying at the surface, the d–d interaction between the same species decreases due to the increase of the neighbour–neighbour distance. This results in an increase in the density of conduction band electrons. This enhanced density of conduction band electrons produces an enhanced exchange interaction, which results in an overall increased energy. Since the Pd 4d band and the Ag 4d band are far apart, it is more likely that the same species gather together to form clusters in order to decrease this energy. Our analyses of these experimental results are consistent with recent results of a STM study of Ag on a Pt(111) surface. They have shown the formation of a Ag cluster embedded in a Pt matrix [28]. Similar phenomena can be found in other systems. A miscibility gap in Co–Pt alloy thin films has been reported [29]. The Co–Pt system also forms a disordered metallic continuous solid solution in the fcc structure at high temperatures. But at the surface, the clustering of Co atoms can be caused by surface equilibrium effects driven by magnetic energy. There could be several reasons for this system not being directly observable by means of XPS, including the broadness of the peak itself. Also, the origin of the phase separation in Co–Pt is quite different from our observation, which has only an electronic origin. The Co 3d band and Pt 5d electrons are located close together, so there will be no significant change in the interaction as we have mentioned above regarding our samples.

In summary, we have shown direct evidence of surface-induced phase separation of a Pd–Ag alloy system at room temperature obtained using high-resolution x-ray photoelectron spectroscopy. These separated phases can be mixed upon heating the sample to 600 °C. This process is reversible but the time constant for the phase separation is relatively large. Also, this phase separation can be accelerated by Ar ion irradiation.

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