PHYSICAL REVIEW B VOLUME 48, NUMBER 11 15 SEPTEMBER 1993-I

Pd-Ti bimetallics: A study of the electronic structure using x-ray photoelectron spectroscopy and x-ray-absorption near-edge structure

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(Received 1 March 1993)

We studied the core-level binding-energy shifts and the valence-band behavior of Pd_3Ti and $PdTi_2$ alloys using x-ray photoelectron spectroscopy (XPS) and x-ray-absorption near-edge structure (XANES). The observed Pd core-level shifts in the alloys, relative to the pure metal, were not consistent with the electronegativity predictions. It is proposed that upon alloying there is an increase in the number of *sp*-like conduction electrons and a decrease in the number of *d* electrons at the Pd site. This electron redistribution at the noble-metal site in the alloy results in a small net charge flow between Pd and Ti, in the direction in accord with electronegativity predictions. Pd L_3-edge and Ti K-edge XANES provide further evidence of electron redistribution upon alloying. Net charge transfer at the Pd site of $PdTi_2$ has been estimated to be 0.29 ± 0.02 electron counts on the basis of a charge compensation model, results from XPS binding-energy shift, and XANES white-line areas. The observed Pd valence-band narrowing and shifts to a higher binding energy are also explained in terms of dilution and charge redistribution.

INTRODUCTION

Many studies have been carried out to investigate the charge redistribution in alloys containing noble metals. It has been shown that in these alloys there is a significant charge redistribution upon alloying.[1-4] Several investigations looked at intermetallic compounds where both constituents had nearly full *d* bands. A study of Au-Ag bimetallics showed a noticeable charge redistribution even though Au and Ag both have full *d* bands and are very close in electronegativity.[5,6] Recently we studied Au-Ti alloys and found that Au gains *sp*-type electrons and loses *d* electrons.[7] Although the electronegativity difference between the two metal constituents is quite large the overall charge flow was quite small in accord with electroneutrality requirements and the observed core-level shifts were of less than 1 eV. In order to see if the trends seen in the Au-Ti system apply to 4*d* noble metals we decided to examine the Pd-Ti alloys.

An investigation of Pd_3Ti and $PdTi_2$ bimetallics using x-ray photoelectron spectroscopy (XPS) and x-ray-absorption near-edge structure (XANES) is described herein. Core-level binding-energy shifts as well as the changes in the valence-band upon alloying are discussed in detail. Our goal was to see if the trends observed in the Au-Ti system would apply to the Pd-Ti system as well. Au and Pd are 5*d* and 4*d* noble metals, respectively, and differ only slightly in electronegativity, yet their *d* bands have different structure and position. The Pd *d* band spreads across the Fermi level and directly overlaps with the Ti valence band. Pd also has narrow unoccupied densities of states at the Fermi level. The *d* band of Au, on the other hand, lies ~5.0 eV below the Fermi level. We want to see if the different positions of the noble-metal *d* bands have any effect on the core-level binding-energy shifts upon alloying. In addition to looking at binding-energy shifts of Pd 3*d* and Ti 2*p* core levels this investigation will also examine the changes in the white-line area of Pd L_3-edge and Ti K-edge XANES, which probe the unoccupied densities of states of *d* and *p* character at the Pd and Ti sites, respectively.

EXPERIMENT

Pure Pd and Ti samples were obtained commercially and came as foil strips. The Pd_3Ti and $PdTi_2$ alloys were made by melting stoichiometric proportions of the two metals and quenching them to room temperature according to the phase diagram.[8] The samples were cleaned *in situ* with Ar^+ ions according to a standard procedure.[7] A wide XPS scan was taken after sputtering to ensure that no surface contaminants (i.e., oxygen and carbon) were present.

The XPS experiments were carried out at Surface Science Western using an SSX-100 x-ray photoelectron spectrometer which contains a monochromatized Al-$K\alpha$ small-spot-size x-ray source. Samples were positioned at a 45° angle of emission with respect to the analyzer lenses. All spectra were obtained with a 300-μm spot size providing an overall spectrometer resolution of ~0.6 eV. A minimum pressure of 4.3×10^{-9} torr inside the spectrometer was maintained during analysis and a pressure of 1.0×10^{-7} torr was used when sputtering. All valence-band spectra were aligned to the Fermi level and normalized to the photon flux. Binding energies are referenced to the Fermi level.

Ti K-edge spectra of $AuTi_3$ and Ti were obtained using thin films prepared from fine powdered samples mixed with Vaseline in a transmission mode at the X-11A Si(111) DCM (double-crystal) beam line of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. Ti K-edge spectra of $PdTi_2$ together with Pd L_3-edge spectra were also obtained at NSLS using the X-23B beam line in a total electron yield mode with a helium detector. The monochromator was detuned to 60% of its maximum intensity at the edge energy. All

XANES spectra were aligned to the point of inflection of the edge and normalized to the edge jump.

RESULTS AND DISCUSSION

XPS core-level binding-energy shifts

Figures 1 and 2, respectively, show the Pd 3*d* and Ti 2*p* XPS spectra for the Pd-Ti bimetallics. Table I summarizes the derived experimental parameters which were obtained by fitting the peaks with a Doniach-Sunjic many-body line shape.

As noted previously, Pd is a 4*d* noble metal with a nearly full *d* band and Ti is an early transition metal with a nearly empty *d* band. Pd is also more electronegative than Ti (according to Pauling's electronegativity table) and as a result one would expect a small charge transfer from Ti to Pd. If that were the case, a negative Pd core-level binding-energy shift (i.e., shift to a lower binding energy) would be anticipated. Ti, on the other hand, should lose electron charge and its core levels should shift towards higher binding energy. Figures 1 and 2 and Table I show that both Pd 3*d* and Ti 2*p* core levels shift toward higher binding energy upon alloying. It seems that the electronegativity prediction is valid for the Ti 2*p* shift but fails to explain the observed Pd 3*d* shift. We show below that this discrepancy can be qualitatively understood in terms of a charge redistribution model.

It has been shown that the binding-energy shift in Pd can be understood on the basis of one-electron energies and electron charge redistribution using the following equation[1]:

$$\Delta E_{\text{Pd}} = -\Delta n_c F_c - \Delta n_d F_d + \delta F_{\text{latt}} + \Delta E_F + [dE/dV]\Delta V \quad (\text{Pd}\rightarrow\text{alloy}) . \quad (1)$$

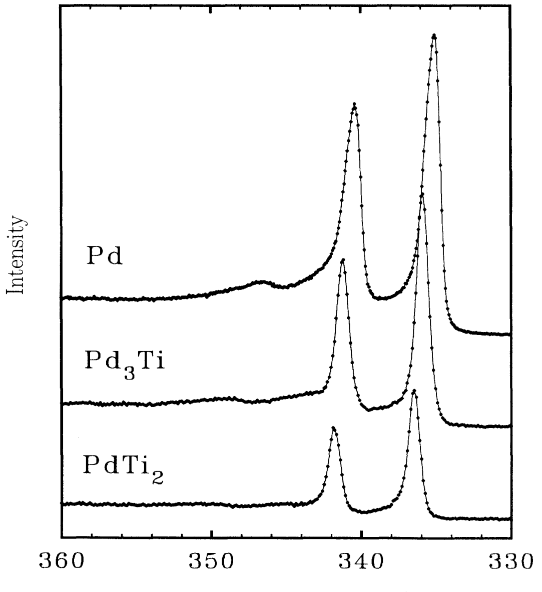

FIG. 1. XPS Pd 3*d* core-level spectra of Pd, Pd_3Ti, and $PdTi_2$.

TABLE I. Relevant experimental parameters.

Sample	ΔE^a Pd $3d_{5/2}$	ΔE^a Pd $3d_{3/2}$	ΔE^a satellite	ΔE^b Ti $2p_{3/2}$	ΔE^b Ti $2p_{1/2}$
Pd_3Ti	0.80	0.81	3.14	0.86	0.85
$PdTi_2$	1.37	1.38	4.07	0.33	0.34

[a] Changes relative to pure Pd in units of eV.
[b] Changes relative to pure Ti in units of eV.

In Eq. (1), ΔE_F is the Fermi-level shift and can also be represented by the work-function change $-\Delta\phi$ to the first approximation. F_c and F_d are Coulomb integrals and represent the interaction of the core electron of interest with the conduction and the *d* electrons, respectively. They represent the changes in the core-electron binding energy resulting from the addition or removal of a single conduction or *d* electron, respectively, at the Pd site. $[dE/dV]\Delta V$ represents volume correction. This term is very small for this system and is neglected in this analysis. It is apparent from Eq. (1) that if we assume the first two terms play a dominant role, as they often do, then for ΔE_{Pd} to be positive as observed, Δn_d must be negative (i.e., Pd is losing *d* charge). Equation (1) can be rearranged to give

$$\Delta E_{\text{Pd}} = -\Delta\phi - \Delta n_c(F_c - F_{\text{latt}}) - \Delta n_d(F_d - F_{\text{latt}}) . \quad (2)$$

Δn_c and Δn_d are non-*d* and *d* charge flow onto and off the Pd site. δ is a small net charge flow onto the Pd site as required by electroneutrality considerations.

$$\delta = \Delta n_c + \Delta n_d . \quad (3)$$

The presence of this charge outside of the Pd Wigner-Seitz volume gives rise to Madelung-like contribution δF_{latt}.[1]

In the past, to gain information from these equations

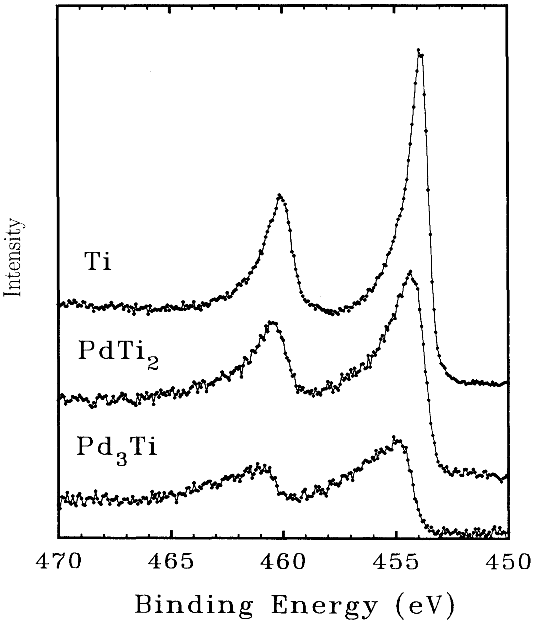

FIG. 2. XPS Ti 2*p* core-level spectra of Ti, $PdTi_2$, and Pd_3Ti.

Mössbauer and XPS data were required. That posed a limitation on the applicability of this model since only a few metals have good Mössbauer nuclei. We show here that by using Δn_d from XANES results this model can be extended to all alloy systems. Using Eqs. (2) and (3) we can estimate the direction and nature of the charge flow between Pd and Ti. The Pd Coulomb integrals are not well known; using the values for F_d and F_c for Ag (Ref. 1) and scaling them to those of Au based on the renormalized scheme,[9] we were able to estimate the corresponding values for Pd.[10] By using the difference in the white-line area in Fig. 3 and the procedure described below and elsewhere[5] we were able to determine the value of Δn_d to be -0.37. Using this value, the work-function change, as well as the estimated Coulomb integrals and $F_{\rm latt}$ (Ref. 10), we were able to calculate the non-d charge flow and the net charge flow onto the Pd site in PdTi$_2$. These results are listed in Table II. It can be seen from Table II that Pd gains the *sp*-type conduction electrons and to compensate for that it loses *d* electrons. Overall, Pd gains more *sp* electrons than it loses *d* electrons. As a result Pd gains negative charge, as indicated by the positive δ value, and so satisfies the electronegativity requirement. The charge compensation works in Pd because Pd $F^0[3d,4d] > F^0[3d,c]$.[10] That produces the positive Pd 3*d* binding-energy shift observed in the experiment. This charge flow can also be looked at as charge redistribution within the Pd atom. There is a net gain in the number of *sp* electrons and a loss of *d* electrons. The *d* electrons are simply redistributed into the *sp* conduction band. This rehybridization is not complete and as a result there is some charge transfer from Ti to Pd. The net charge transferred is around 0.3 electrons.

As a result of the charge transfer to Pd, Ti becomes slightly positive upon alloying with Pd. Since the corresponding Coulomb integrals in Ti are expected to have similar magnitude, a positive binding-energy shift for its core levels would be expected based on the charge-compensation model.[1] Figure 2 shows that Ti 2*p* core levels do indeed shift to a higher binding energy upon dilution of Ti in Pd.

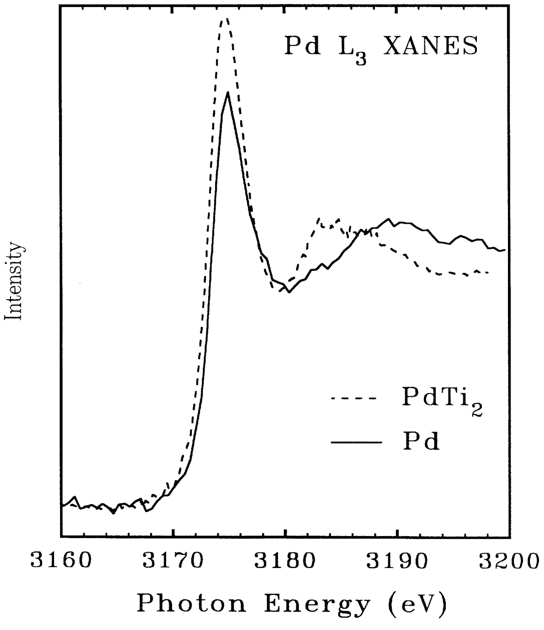

FIG. 3. Normalized Pd L_3-edge XANES of Pd and PdTi$_2$. All spectra are aligned to the edge jump.

TABLE II. Charge redistribution in PdTi$_2$ relative to pure Pd.

Alloy	ΔE_B (eV)	$\Delta\phi$[a] (eV)	δ[b]	Δn_c	Δn_d	$\Delta n_c/\Delta n_d$
PdTi$_2$	1.37	−0.53	0.29	0.67	−0.37	−1.8

[a] Reference 10.

[b] Calculated using Eq. (3) given in the text.

[c] All values are relative to pure Pd.

The Pd 3*d* satellite, shown in Fig. 1, shifts towards higher binding energy and diminishes in intensity upon alloying. This satellite represents either an extra atomic electron energy loss or a shakeup process where electrons from the Pd *d* band are excited into some state of *nl* character above the Fermi level. The latter is more likely since no such satellites are observed in the Ti 2*p* spectrum. A decrease in intensity of the satellite and the shift toward a higher E_B indicates that the *nl* state in Pd has moved away from the Fermi level and the Pd *d* band in alloys with Ti is more localized and more deeply bound. The asymmetric factor of the Pd 3*d* peak also drops significantly from Pd metal to the alloy as seen in Fig. 1. This indicated that the Pd *d* densities of states have moved away from the Fermi level.

The Ti 2*p* core levels exhibit large asymmetry factors and linewidths which are probably due to an increase of *d*-like electron states at the Fermi level, although contribution from slightly different surface Ti sites cannot be eliminated. The asymmetry of the Ti 2*p* line shape increases (see Fig. 2) upon alloying with Pd. This suggests that Ti may be gaining *d* charge at the Fermi level.

XPS valence-band spectra

The normalized valence-band spectra are shown in Fig. 4 where several features can be clearly seen. First, the alloy valence band is dominated by the Pd *d*-band components which have a high cross section. Second, there is a significant narrowing in the valence band as well as a shift away from the Fermi level. The positive E_B shift can be easily explained in terms of *s*-*d* rehybridization. The valence-band shift is expected to be in the same direction as the core levels.

The narrowing of the Pd *d* band upon alloying is a result of the interplay of dilution and spin-orbit splitting. The *d*-*d* interaction between Pd atoms in the alloy is significantly less than in a pure Pd. The width of the *d* band is approximately proportional to the square root of the coordination number of Pd atoms.[11] The farther apart the atoms are, the narrower the valence band becomes. The palladium *d*-band narrowing is quite substantial and it is also indicative of the small *d*-*d* interaction between Pd via Ti.

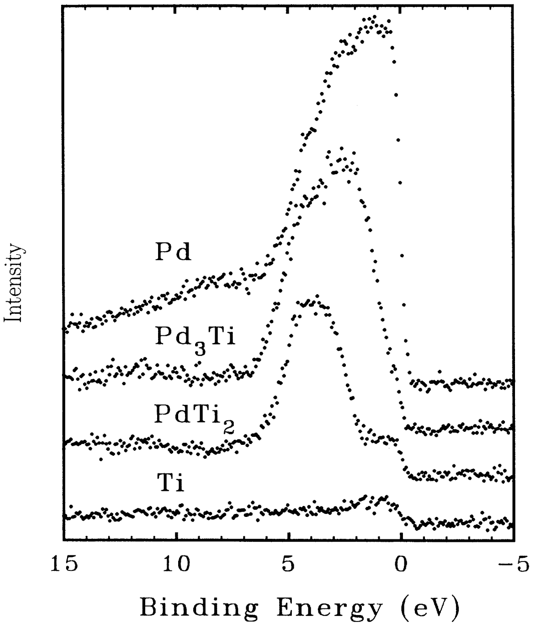

FIG. 4. XPS valence-band spectra of Ti, $PdTi_2$, Pd_3Ti, and Pd. All spectra are normalized to the photon flux and aligned to the Fermi level.

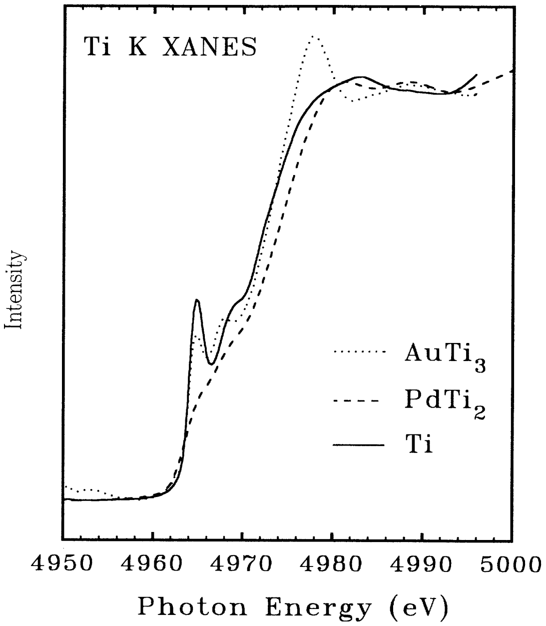

FIG. 5. Normalized Ti K-edge XANES of Ti, $AuTi_3$, and $PdTi_2$. All spectra are aligned to the edge jump.

Finally, it is interesting to note that the intensity of the band just below the Fermi level, well separated from the Pd *d*-band component, is relatively strong when compared with that of pure Ti. This band may be due to Pd-Ti *d*-*d* interaction which increases the *d* character at the Ti site at the Fermi level. This is in accord with the increase in the asymmetry of the Ti 2*p* core levels.

XANES

It has been demonstrated that the XANES technique exhibits great sensitivity in probing minute changes in the unoccupied density of states above the Fermi level.[5,12] We used this technique here to substantiate the conclusion from the XPS results. Figure 3 shows the Pd L_3-edge XANES obtained for Pd and $PdTi_2$. It is immediately evident from the figure that there is a substantial increase in the white-line area of $PdTi_2$. Since the Pd L_3-edge probes the $2p_{3/2} \rightarrow d_{5/2,3/2}$ dipole transition in Pd, the increase in the area under the white line represents an increase in the unoccupied densities of states of *d* character above E_F.[13,14] This, in turn, implies a decrease in *d*-electron count at the Pd site in the alloy and provides an independent proof that Pd loses *d* charge upon alloying with Ti. Similar results were obtained with Pd L_2-edge XANES. Analysis of these data relates the area under the white line to the number of *d* holes. We first compare the white line of pure Pd with that of pure Ag. The difference in the white-line areas accounts for the difference in *d*-hole counts given by the band structure.[15] The area under the white line in the alloy is then scaled accordingly to the *d*-hole count of the Pd metal.

Ti *K*-edge XANES, seen in Fig. 5, provides us with a look at the Ti site in the alloy. Here the pre-edge region corresponds to the normally forbidden $s \rightarrow d$ dipole transition. The decrease in intensity observed following alloy formation indicates that Ti gains *d* charge.

CONCLUSION

The Pd 3*d* core-level binding-energy shifts in Pd-Ti alloys, which seemed to oppose the electronegativity predictions at first glance, were explained using a charge-compensation mechanism in which Pd gains *sp*-type conduction electrons and loses *d* electrons. The charge redistribution, however, is not complete and as a result there is a small net charge flow δ from Ti to the Pd site in accord with the electronegativity arguments. This behavior seems to be general for 4*d* and 5*d* noble-metal–early-transition-metal bimetallics. The depletion of the *d* character is also evident from the decrease in the *d*-band intensity upon bond formation and the fact that the *d*-band shifts away from the Fermi level. The dilution effect reduces Pd *d*-*d* interaction and is responsible for the *d*-band narrowing. Both L_3-edge and *K*-edge XANES results confirm the depletion of *d* charge at the Pd site and the increase of *d* charge at the Ti site upon alloying. Thus it appears that Pd loses *d* charge and this is overcompensated by a gain in non-*d* charge while Ti gains *d* charge and this gain is at the expense of a greater loss in non-*d* charge count. The overall charge flow is in agreement with electronegativity arguments. We showed that this model can be used for systems where Mössbauer data are not available.

ACKNOWLEDGMENTS

We would like to thank Walter Kunnmann of the Brookhaven National Laboratory for preparing the alloys. Research at UWO was supported by the Ontario Centre for Materials Research (OCMR) and the Natural Sciences and Engineering Research Council of Canada (NSERC). NSLS is supported by the U.S. Department of Energy. We would also like to thank M. Kuhn and R. Sammynaiken for some of the XANES measurements.

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