

Metal-Ceramic Interface Adhesion: Band Structure Calculations on Pt-NiO Couples

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Received October 6, 1992. Revised Manuscript Received January 15, 1993

Under certain annealing conditions Pt-NiO couples form NiPt intermetallic layers at the interface. It has been suggested that an observed 4-fold increase in the ultimate shear strength of the interface upon inclusion of a 1-nm-thick NiPt interlayer is caused by metal-oxygen bonding at the interface. Extended Hückel calculations, within the tight-binding formalism, have been performed on a series of Pt- and NiPt-NiO metal-ceramic couples to elucidate the nature of the bonding at these interfaces. The calculations showed an approximately 5-fold increase in adhesion energy in NiPt-NiO over Pt-NiO. This is attributed to the more efficient electron donating capability of nickel compared to that of platinum. Bonding across the interface is found to decrease with increased electron donation as interfacially antibonding orbitals are filled. Theoretical reasons for the eventual mechanical failure in the oxide component are adduced.

A problem of critical technological importance and fundamental scientific interest in materials science and materials engineering is that of adhesion between metals and ceramics. Metal-ceramic adhesion is important to such industrial areas as microelectronics, catalysts, protective coatings for metals and metal-ceramic composite materials. As recent reviews of the subject indicate,^{1,2} a better understanding of the fundamental factors that affect metal-ceramic adhesion would not only aid in the development of new industrial products and processes, but would open up new areas of research as well.

Venkataraman et al. determined the work of adhesion for Pt thin films on NiO by a continuous microscratch technique and reported a lower bound of 0.047 J/m² for the work of adhesion.³ Shieu et al. examined the use of interfacial reactions for the control of structure and shear strength of metal-ceramic interfaces in the NiO-Pt system.⁴ A platinum plate with a thin NiO film was deformed in tension and examined with scanning electron microscopy (SEM) for the development of cracks in the NiO film. The ultimate shear strength of the interface was determined with the periodic cracking technique of Agrawal and Raj.⁵ The results showed that the formation of a layer of NiPt at the NiO-Pt interface can be controlled by choice of annealing temperature, time, and oxygen partial pressure. Furthermore, the introduction of a 1-nm-thick NiPt layer increased the observed interfacial shear strength by at least a factor of 4. The authors proposed an explanation of the observed adhesion enhancement based on a simple bonding model. It was assumed that the commensurate metal-NiO interfaces had metals positioned directly over the oxygens and that the NiPt, composed of alternating layers of nickel and platinum, was oriented such that nickel atoms were directly over oxygens at the interface, Figure 1. The enhanced adhesion

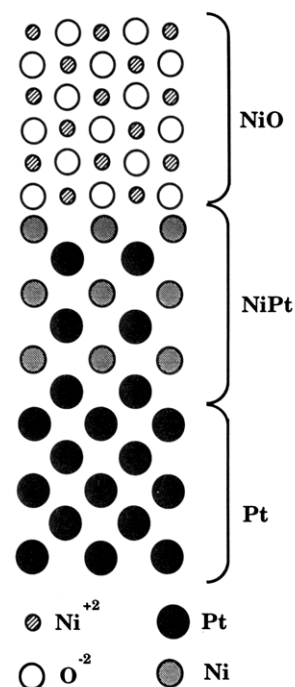


Figure 1. Interface bonding model after Shieu et al. showing orientation of the NiPt intermetallic layer at the interface of Pt and NiO.

was then simply explained as due to the relatively higher strength of the Ni-O bond compared to the Pt-O bond. While this qualitative explanation is intuitively appealing, other factors (structural and electronic) are undoubtedly involved. In this paper we provide a more detailed description of the metal of nickel oxide bonding using band structure calculations.

The extended Hückel calculation method has been outlined and reviewed.^{6,7} This method is particularly well

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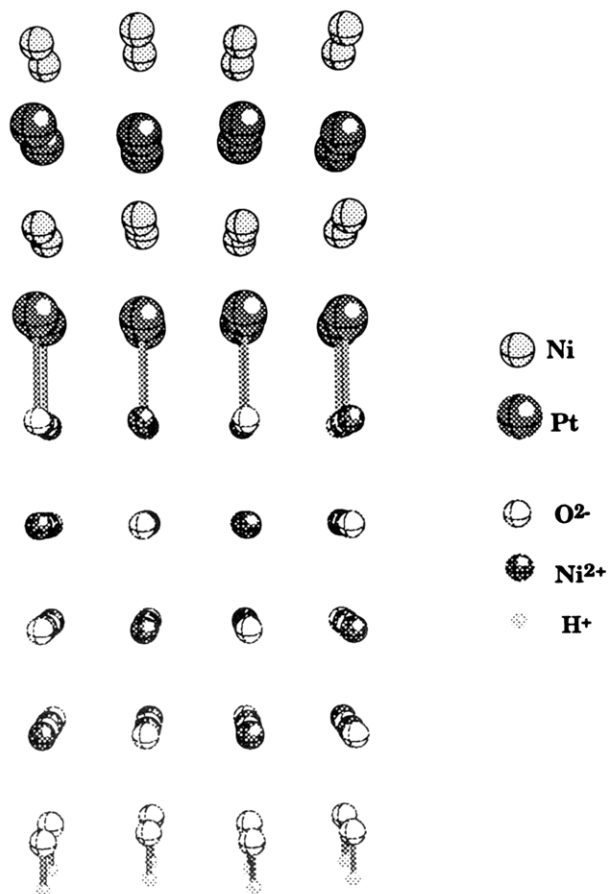


Figure 2. Structure of the NiPt-NiO unit cell showing a four-layer NiPt slab on a four-layer NiO slab with terminating OH functionalities on the noninteracting surface.

suiting to model the extended, two-dimensional nature of interfaces and to study the effect of variations in interface geometry on the overall energy of a structure, as demonstrated in recent calculations on the $(\text{Cr}/\text{Al})_2\text{O}_3/\text{Cr}$ metal oxide metal system.⁸

Specifically, this molecular orbital method allows calculation of the overlap population (an index of bond strength) for the interface. Calibration of such bond strength indices is possible by comparison with similar calculations performed on bulk materials. In addition, the binding energy of the interface is available from comparison of the calculated energy of the separated metal and ceramic surfaces with the calculated energy of the metal-ceramic interface; $\Delta E = E_{\text{couple}} - (E_{\text{met}} + E_{\text{cer}})$, a negative ΔE value denoting net stabilization. Both the magnitude of the overlap population and ΔE can be used to follow trends in interface strength and correlation with adhesion measurements. A more complete discussion of the application of extended Hückel calculations to the study of adhesion is presented elsewhere.⁹

Calculations

Individual metal and NiO slabs were modeled using four-layer unit cells, which were propagated in two dimensions. The metal slabs had two atoms per layer in the unit cell

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Table I. Results From Metal-NiO Couples, Metal over Oxygens at Interface

couple	Fermi level (eV)	ΔE (J/m ²)	charge transfer (e ⁻ /Ni in NiO)
PtNiO	-10.14	- 1.7	0.95
NiPt ₃ NiO ^a	- 9.83	- 8.7	1.50
NiPtNiO	- 9.55	-11.0	1.71
NiNiO	- 9.41	-12.4	1.80

^a An alloy slab with one layer of Ni atoms directly above the interface.

while NiO contained two nickels and two oxygens per layer in the unit cell. Metal-NiO couples were studied using 8-layer unit cells, 16–20 Å thick (Figure 2). The separation between the faces forming the interface was set at 2.0 Å for couples with metals positioned directly over oxygens across the interface, and at 2.5 Å for couples with metals directly over nickel. The interface separation distances were chosen as representative of Ni-O and Ni-metal bond distances (from bulk NiO and nickel metal¹⁰), respectively. The noninteracting face of all NiO slabs was terminated with O-H groups over the exposed nickel atoms, so as to remove electron accepting states from this surface. Specific details of the calculations are given in the Appendix.

Results and Discussion

Table I shows the Fermi level, ΔE , and charge-transfer values for the metal-NiO couples with metals positioned directly over oxygens at the interface. In all cases the electron transfer computed is from the metal to the NiO slab. The negative ΔE values indicate that formation of the interface is energetically favorable.

The density-of-states (DOS) curve for NiO, Figure 3c, shows a mainly O_{2p} band extending from -17.0 to -14.5 eV. Two bands, from -14.5 to -12.0 eV and from -12.0 to -8.0 eV, respectively, are primarily nickel in character and can be formally described as the t_{2g} and e_g bands of the octahedrally coordinated nickel. From the DOS curve in Figure 3c, we see that the Fermi level is located at -10.7 eV for Ni²⁺, giving a half-filled e_g band. Thus, NiO would be predicted to be a metallic compound, in clear contradiction with experiments, which show it to be a magnetic insulator. It has been known for some time that the delocalized energy-band formalism fails to properly describe the electronic structure of transition metal oxides, and NiO, a Mott-Hubbard insulator, has been widely cited as an example of this failure.¹¹⁻¹³ Some discussion of the validity of the Mott-Hubbard insulator description of NiO may be found in the recent literature.¹⁴⁻¹⁶ Nickel d orbitals have poor overlap with neighboring atoms giving rise to relatively narrow bands. In such situations the electrons are better described as being in localized states, similar to those found in isolated molecules. The behavior of electrons in these states differs from those in bands, and it is this difference that is at the heart of the failure of band-theory's description of these compounds.

Will these well-known complications in the description of the isolated oxides electronic states affect our descrip-

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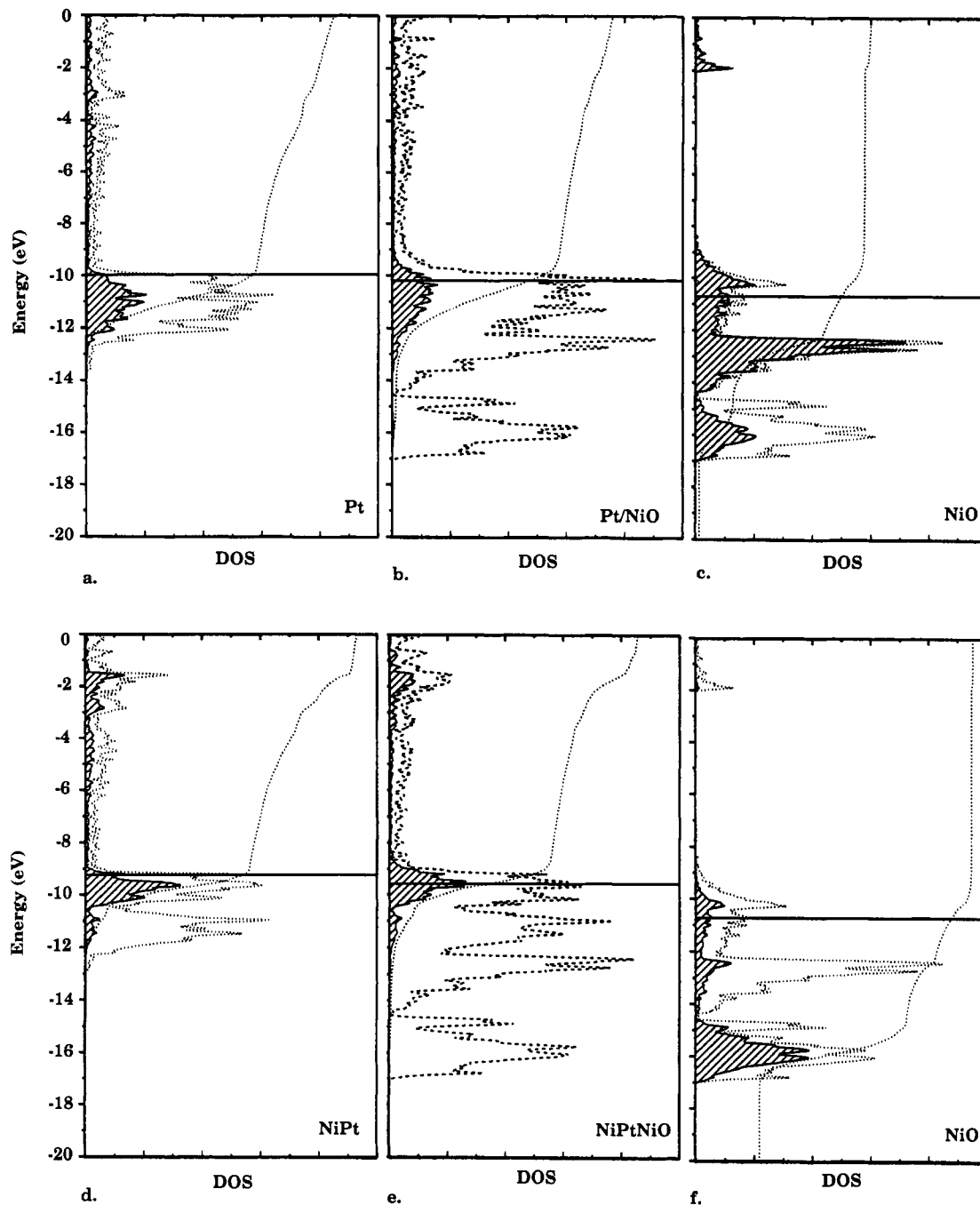


Figure 3. Density of states (DOS) plots for (a) Pt slab, (b) Pt-NiO couple, (c) and (f) NiO slab, (d) NiPt slab, and (e) NiPt-NiO couple. The solid line across each plot indicates the Fermi level. The dotted line gives the integration of the projected DOS: a) Pt atoms at the surface, (b) Pt atoms at the interface, (c) all Ni atoms in the slab, (d) Ni atoms at the surface, (e) Ni atoms at the interface, and (f) all oxygens in the slab.

tion, which is inherently a delocalized one? Our argument will depend crucially on the electron acceptor role played by the e_g states in the formation of NiO-metal couples. The problem of describing conductivity in NiO will not come up directly, and we think that the delocalized band description of the interface may continue to be used.

The platinum DOS, Figure 3a, is typical of a transition metal with a d band between -13.0 and -9.5 eV. The more dispersed s and p bands partially penetrate the d band, extending from -12.5 eV to much higher energies than those in our window. Platinum is a d^{10} metal, and the Fermi level is located close to the top of the d band, at -10.0 eV. The DOS plot of the interacted Pt-NiO couple is shown in Figure 3b with the shaded area indicating the contribution of platinum atoms at the interface. The

resultant band structure shows a slight lowering of the Fermi level to -10.1 eV. The integration of the projected platinum atoms shows very little change in the band structure, except for a small amount of added density at -16.0 eV from interaction with the surface oxygens of the oxide. The DOS curve for the NiPt alloy slab is given in Figure 3d. Two bands have replaced the single d band seen in the platinum DOS. The lower band, from -12.0 to -10.5 eV, is largely platinum in character and the upper band, from -10.5 to -9.0 , is mostly nickel. The Fermi level, at -9.23 eV, is higher than that of the pure platinum metal slab. The interacted NiPt-NiO DOS (Figure 3e) again shows a lowering of the Fermi level to -9.55 eV. A small amount of nickel metal density from the metal layer

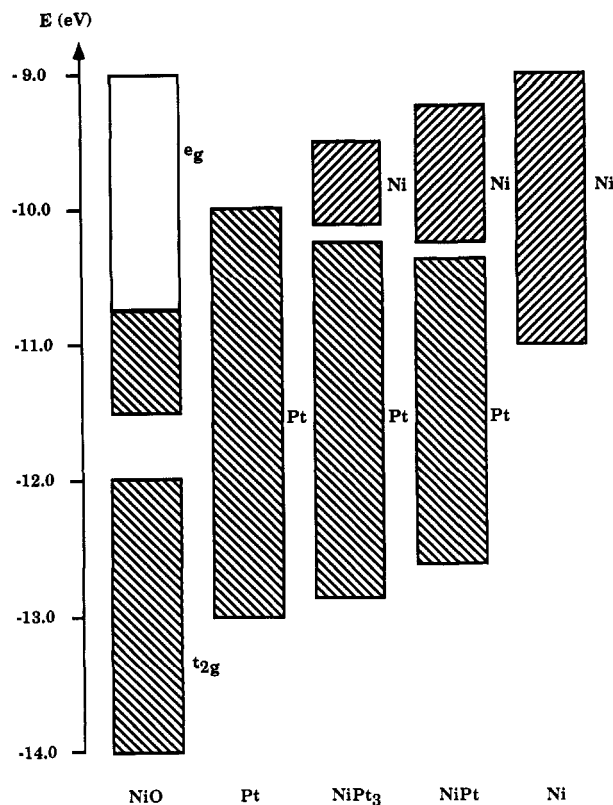


Figure 4. Schematic energy level diagram of the Fermi level region of NiO and metal slabs. The major component of each band is indicated.

Table II. Results from NiPt Intermetallics of Various Orientations

couple	Fermi level (eV)	ΔE (J/m ²)	charge transfer (e ⁻ /Ni in NiO)	% Ni
NiPt–NiO	-9.55	-11.0	1.71	100
mNiPt–NiO	-9.57	- 9.9	1.70	50
PtNi–NiO	-9.59	- 8.8	1.69	0
NiPt–NiO ^a	-9.62	-10.5	1.71	100
mNiPt–NiO ^a	-9.65	-10.5	1.70	50
PtNi–NiO ^a	-9.62	-10.5	1.71	0

^a Couples with an interfacial distance of 10 Å.

at the interface is seen at -16.0 eV, indicating an interaction with the oxygen atoms exposed at the surface.

The data in Table I indicate that the magnitude of ΔE increases with increasing nickel content in the metal slab, i.e., Pt < NiPt₃ < NiPt < Ni. The charge transfer values reflect this same trend, and we can understand the relation of these two parameters through a simplified energy diagram of the Fermi level region shown in Figure 4. Upon interaction of the slabs, electrons are transferred from the higher energy states at the top of the metal d bands to lower energy states in the nickel e_g band of the oxide. This charge transfer stabilizes the system and contributes significantly to ΔE . The increase in ΔE and charge transfer in the metal series is traced to the increase in Fermi level caused by the introduction of higher lying nickel metal states at the interface. Electrons are transferred from these states, yielding more stabilization of the system per electron than for the case of platinum. Moreover, the nickel bands in NiPt₃ and NiPt are relatively narrow and thus there is a higher density of filled states in these bands. The net result is a greater number of higher energy electrons transferred to lower NiO states in the NiPt–NiO

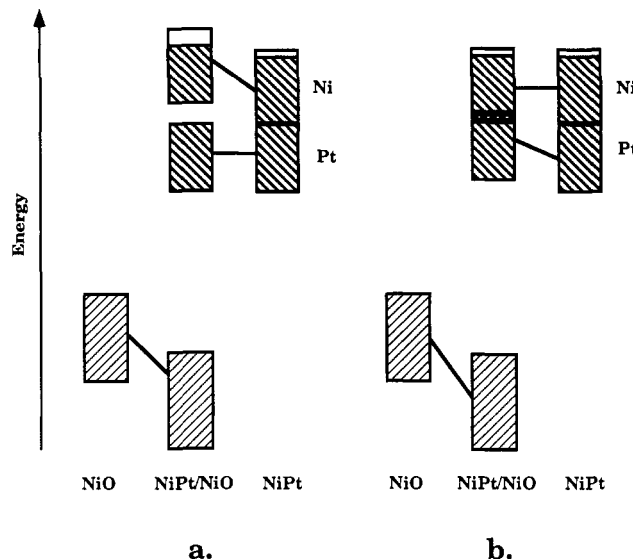


Figure 5. Schematic interaction diagram of the O_{2p} band of NiO with (a) the Ni band and (b) the Pt band of NiPt.

couple than in the Pt–NiO couple. This electron transfer creates the 5-fold increase in ΔE .

It should be noted that the magnitudes of ΔE and charge transfer are unrealistically large. An overestimation of the ionic term (charge transfer between slabs with all covalent interactions “switched off”) causes energies of interaction between materials of very different ionization potentials to be too large. In order to assess the contribution of ΔE arising from the charge transfer alone, calculations were performed on metal–oxide couples with an interfacial separation distance of 10.0 Å (see Table II). At this separation there is no covalent interaction, i.e., there is no bonding across the interface, and all of the stabilization is derived from the nonphysical charge transfer inherent in the method of calculation. It is found that charge transfer accounts for 85 to 95% of ΔE and that the covalent contributions to ΔE range from 0.1 to 1.0 eV in magnitude. The “real” adhesion energy includes some ionic or charge transfer contribution but its magnitude is difficult to assess. Since the relative ionic contribution is constant, we can safely assume that comparisons among various metal–oxide couples will be valid.

To test the assumptions made pertaining to the orientation of the NiPt alloy layer,⁴ a series of calculations attempted to determine whether it is correct to assume that there is a nickel layer directly above the NiPt–NiO interface. Table II shows the results of three calculations of NiPt–NiO couples used to address this question. “mNiPt” is a “random” distribution of nickel and platinum in the alloy with one atom of each type per layer in a unit cell. “PtNi” has the same structure as NiPt but with a platinum layer at the interface. The energy per unit cell and band structure of the individual alloy slabs was the same, and in all three cases the calculations were performed with metals over oxygens at the interface. The results show that ΔE values scale linearly with the percentage of nickel in the metal layer at the interface. The charge transfer and Fermi level values also scale linearly with nickel content but do not show substantial changes.

The foregoing observations suggest that the change in ΔE is not a purely “ionic” effect, i.e., not only charge transfer; a conclusion further supported by calculations

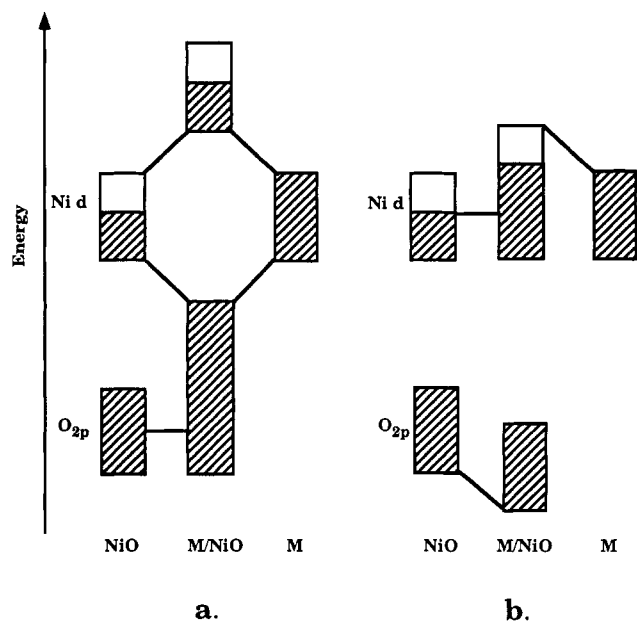


Figure 6. Schematic diagram of the interaction of a metal slab with (a) the Ni e_g band and (b) the O $2p$ band of NiO.

on NiPt-NiO and PtNi-NiO couples with interfacial separation distances of 10 Å (Table II). Both couples have a ΔE value of -10.5 eV, which is a product of charge transfer alone since the overlap population across the 10 Å interface is zero. Comparison to the ΔE values of the 2.0 Å interfacial separation couples indicates that the covalent contribution to ΔE is negative (or attractive) in the case of nickel at the interface and is positive (or repulsive) with platinum above the interface. An analysis of the covalent interaction from the DOS plots reveals the cause of this difference. The interaction in each case is schematically illustrated in Figure 5. The interaction of nickel atoms of the alloy with oxygens of the oxide (Figure 5a) produces an increase and decrease in their respective band energies, resulting in an emptying of higher energy nickel metal states as they are moved above the Fermi level. This covalent interaction results in a net attraction. The interaction of platinum atoms with oxygens (Figure 5b) does not result in the same emptying of high energy metal states since the platinum states are still below the Fermi level. It produces a net repulsion similar to a closed shell, "four-electron" interaction of discrete molecular energy levels. Thus, the original assumption of a nickel metal layer directly over the NiO does correspond to an energetically preferable configuration.⁴

To address whether the metal-oxide interfaces are oriented so as to have the metal atoms over oxygen or nickel ions, all of the couples shown in Table I were recalculated with metals positioned directly over nickel atoms at the interface and with an interfacial separation distance of 2.5 Å. There was no clear trend in the magnitude of adhesion enhancement, $\Delta E_{M-O} - \Delta E_{M-Ni}$, for the series, which ranged from 0.1 to 1.7 eV. In all cases the Fermi level was lower and the adhesion was enhanced when the metal was positioned over nickel, in spite of the greater interfacial separation. This adhesion enhancement indicates that the assumed geometry of metal over oxygen⁴ is no better than that of a metal over nickel configuration and, in some cases, is energetically less favorable. These results are a consequence of a better energy match for interaction between the metals and the nickel (Figure 6a)

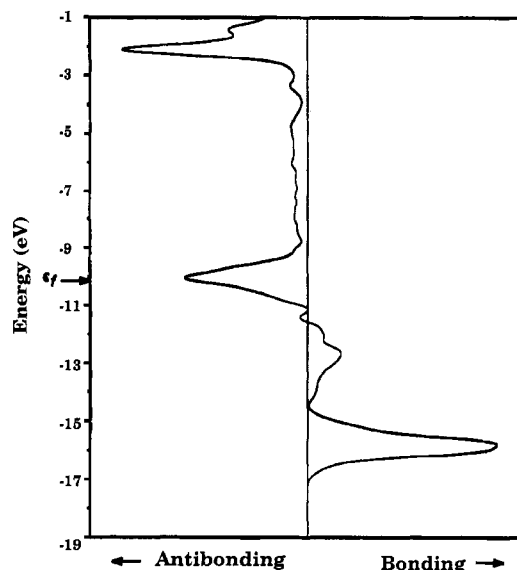


Figure 7. COOP plot of Pt-O bonds across a Pt-NiO interface with metals situated directly over oxygens.

than for the metals and the oxygens (Figure 6b), resulting in a greater overall stabilization.

In interfaces between transition metals and Al_2O_3 , interface overlap populations (IOP) were used as a measure of bonding across the interface.^{8,9} These bonding indices were found to be proportional to ΔE values, suggesting a strong link between adhesion energy and atom-to-atom bonding across the interface. One difficulty in the use of IOP as a measure of adhesion strength is that comparisons between different types of bonds, i.e., Ni-O and Pt-O, cannot be made. Some direct comparisons of IOP can be made in the metal-NiO series. For instance, the trend in IOP of Ni-O bonds is, NiPt₃NiO > mNiPtNiO > NiPtNiO > NiNiO. For Pt-O bonds it is, PtNiO > PtNiNiO = mNiPtNiO. In both cases the trend in IOP is opposite to variations in ΔE and in charge transfer. This can be understood in terms of the filling of interfacially *anti-bonding* orbitals as electron transfer increases. The effect is evident in the Pt-O IOP plot of the Pt-NiO interface (Figure 7), where the Fermi level lies in the middle of a strongly antibonding band. Further electron donation from the metal to the oxide will include donation to this antibonding band and result in smaller IOP values.

An issue of considerable practical importance is that of *where* the interface fails when decohesion occurs. Failure could occur inside the metal, inside the ceramic, or right at the interface. While an accurate prediction of the locus of failure in a specific metal-ceramic couple is not yet possible, an idea of the changes in chemical bonding that occur within the metal or oxide slabs upon formation of the interface can be obtained from the calculations. The strengthening or weakening of chemical bonds within the metal or oxide slabs can have a profound effect on the practical work of adhesion. Bonding inside the NiO slabs, estimated from crystal orbital overlap population (COOP) analysis, decreases upon interaction with the metal in all cases studied. Electrons transferred from the metal to the NiO are transferred to the nickel e_g band, made up of locally Ni-O antibonding states. Ni-O bonds in the oxide slab are weakened as a consequence. The greater the electron transfer, the greater is the weakening of the bonding in the oxide. Conversely, since both nickel and platinum are d^{10} metals, the electrons transferred to the

Table III. Extended Hückel Parameters

atom	orbital	H_{ii} , eV	ζ_1	ζ_2	c_1	c_2
H ²¹	1s	-13.60	1.30			
O ²¹	2s	-32.30	2.28			
	2p	-14.80	2.28			
Ni ²³	4s	-9.17	1.83			
	4p	-5.15	1.13			
	3d	-13.39	5.75	2.00	0.57	0.63
Ni ^{24 a}	4s	-7.80	2.10			
	4p	-3.70	2.10			
	3d	-9.90	5.75	2.00	0.57	0.63
Pt ²⁵	6s	-9.15	2.55			
	6p	-4.38	2.55			
	5d	-11.00	6.01	2.70	0.63	0.55

^a Parameters used for Ni in metal slabs.

oxide are removed from M-M antibonding orbitals. Bonding within the metal slab, as indicated by our COOP analysis, then increases. One exception to this enhanced bonding is M-M bonding within the layer directly over the interface, which, in most cases, is weakened after interaction. This is related to a similar effect seen in catalyst-adsorbate interactions;⁷ bonding between the adsorbate and the surface is created at the expense of bonding within the molecule itself. In our case, bonding within the first layer is the net result of the competition between removal of electrons from antibonding orbitals and weakening of the bonds from interaction with the NiO layer directly below.

Summary and Conclusions

In spite of the simplicity of the model and the approximate computational techniques, some general conclusions concerning adhesion and bonding in these metal-ceramic couples can be made. A simple electron-transfer model indicates how ΔE and charge transfer increase with increasing nickel content of the intermetallic phase, due to the greater efficiency of electron transfer from the nickel states that are higher in energy than the platinum states. The 4.7-fold increase in ΔE from Pt-NiO to NiPtNiO interfaces, calculated using an average of all geometries, correlates well with the experimentally observed 4-fold increase in ultimate shear strength of the NiPt containing interface.

The interface overlap population, a measure of bond strength, was found to scale *inversely* with ΔE due to electron transfer to interfacially antibonding states. Thus, caution must be exercised with the use of IOP as a measure

of adhesion strength.

Exploration of the influence of interfacial geometry revealed that M-Ni, rather than M-O bonding is preferred. A nickel layer directly above the NiO is energetically favored over a platinum layer.

COOP analysis of the bonding inside the interacting slabs showed a general weakening of the oxide and strengthening of the metal. Both effects are the consequence of electron transfer from locally antibonding orbitals of metals having high d-electron counts to antibonding e_g orbitals of NiO. Thus, it is suggested that failure should occur in the oxide.

Acknowledgment. The stay of P.A. at Cornell University has been made possible through a postdoctoral grant of the Ministerio de Educación y Ciencia of Spain. R.S.B. was supported under a DOE fellowship, and this work was supported by the MRL Program of the National Science Foundation under Award No. DMR-9121654.

Appendix

All calculations were of the tight-binding¹⁷⁻¹⁹ extended Hückel type.^{20,21} Extended Hückel parameters used in all calculations are listed in Table III. Platinum, nickel, and NiO share the *Fm3m* space group;¹⁰ platinum has the Cu structure with $a = 3.923$ Å, nickel has the Cu structure with $a = 3.535$ Å, and NiO has the NaCl structure with $a = 4.194$ Å. A low temperature phase of NiPt, space group *P4/mmm*, AuCu structure, $a = 3.821$ Å, $c = 3.591$ Å was used. To obtain commensurate interfaces, the unit cell parameter a was set at 4.0 Å for all calculations. Unit cell parameter c was retained at 3.591 for NiPt slabs. In all calculations, 28 k points were used in the irreducible portion of the BZ. k point sets were chosen by the method of Ramírez and Böhm.²²

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