

SURFACE SCIENCE LETTERS

**CO DISSOCIATION ON Ni–Zr ALLOYS STUDIED BY
PHOTOEMISSION AND ELECTRONIC STRUCTURE CALCULATIONS**

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We present a photoemission study of the CO adsorption on amorphous Ni–Zr alloys at various compositions. Our results indicate a distinct enhancement of dissociative adsorption even at very low Zr concentrations. These observations are supported by LCAO-type calculations of potential energy surfaces, which suggest a strong increase of backdonation into antibonding CO $2\pi^*$ type orbitals near Zr sites.

The dissociative chemisorption of CO on transition metals (TM's) is an important step, which, depending on the reaction conditions, can become rate limiting in catalytic processes such as the Fischer–Tropsch synthesis [1]. The selection of the optimum catalyst is based on the fact that early TM's (TM's with a less than half filled d-electron shell) tend to dissociate CO (and get fast poisoned by the reaction products), while mainly molecular CO adsorption is observed on late TM's (TM's with a more than half filled d-electron shell) at room temperature [2]. Since a large group of metallic glasses (MG's) are alloys of early and late TM's, the possibility of their use as catalysts attracts much interest [3]. These materials are stable over a very large composition range and show in general no structural or electronic heterogeneities. The possibility of fine tuning the electronic and geometric structure in MG's allows for an optimization of their catalytic activity and selectivity and a minimization of their self-poisoning tendency.

In this letter we present an investigation of the dissociative CO adsorption on amorphous TM alloys. We chose $\text{Ni}_x\text{Zr}_{1-x}$ alloys which are stable in the

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glassy state in a wide composition range and which have been intensively studied previously [3–5]. The ability of these alloys to dissociate CO under different conditions was studied by ultraviolet photoemission spectroscopy (UPS) and by calculating potential energy surfaces for the dissociative CO adsorption in a realistic geometry near step sites for different alloy compositions.

The Ni-Zr Mg's were prepared by rapid quenching from the liquid state in high vacuum by using either a magnetic two piston apparatus with RF levitation melting, or a melt spinning equipment. The amorphous state of the samples was checked by X-ray diffraction. The surfaces were cleaned by Ar-ion sputtering or by mechanical cleaning with a tungsten brush before exposing the samples to high purity CO. No sputtering-induced surface segregation could be detected by core level XPS. The UPS He II measurements were performed in a Leybold-Heraeus spectrometer (EA 10/100) by operating the analyzer in the constant pass energy mode ($E_{sp} = 20$ eV) with an energy resolution of 0.25 eV at a residual gas pressure in the 01^{-11} mbar range and a He gas pressure of the order of 5×10^{-9} mbar. All spectra were recorded 30 s after CO exposure and the measuring time for each spectrum was 10 min.

The CO chemisorption behavior of glassy $Ni_{64}Zr_{36}$ at 80 K is demonstrated by the UPS He II ($E_{ph} = 40.8$ eV) valence band spectra in fig. 1. The spectrum of the clean glassy $Ni_{64}Zr_{36}$ (see fig. 1a) is dominated by a valence band formed by Ni 3d and Zr 4d electron states. An interesting aspect of glassy alloys of early and late TM is a concentration dependent shift of the late TM (Ni)-derived d states towards higher binding energies, accompanied by a shift of the early TM (Zr)-derived d states towards lower binding energy, thereby enhancing their contribution to the density of states (DOS) at E_F [4,5]. The spectrum obtained after chemisorption of 8 L CO at 80 K exhibits basically

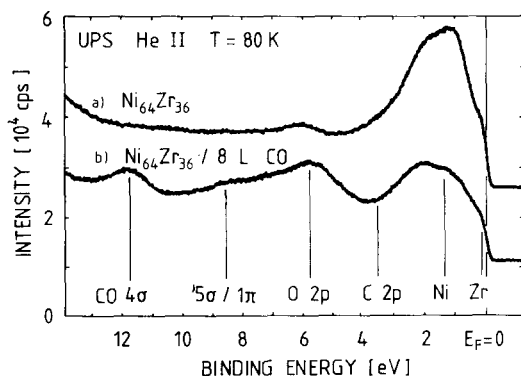


Fig. 1. UPS He II ($E_{ph} = 40.8$ eV) valence band spectra at room temperature of clean and CO exposed surfaces of glassy $Ni_{64}Zr_{36}$ alloys.

three additional peaks at binding energies of about 11.5, 8.5 and 5.5 eV which contain information about the amount of molecular and dissociative CO chemisorption. In fact, the peaks at 11.5 and 8.5 eV correspond to the 4σ and the unresolved $5\sigma/1\pi$ orbitals of the CO molecule, whereas the presence of oxygen stemming from CO dissociation is shown unambiguously by the O 2p peak close to 5.5 eV. The flat maximum at 6.0 eV in the $\text{Ni}_{64}\text{Zr}_{36}$ spectrum (curve a) results at least partly from a satellite, which is also present at clean Ni surfaces, and is not only caused by oxygen contamination [6]. The C 2p structure is located close to the bottom of the d-valence band and cannot be resolved.

In the following we report on the chemisorption properties of glassy Ni–Zr alloys by studying the CO 4 area corresponding to the molecular state and the O 2p peak height corresponding to the dissociative adsorption as a function of temperature and alloy concentration. Each data point of fig. 2 has been obtained by adsorbing 8 L CO (saturation coverage) on a clean substrate at a given temperature. On pure Zr, CO is adsorbed dissociatively for $T > 80$ K. As shown in fig. 2a, pure Ni adsorbs CO in a molecular state at low temperatures. Increasing the temperature causes a decrease of the amount of molecularly adsorbed CO due to desorption. Although CO is known to dissociate near ion bombardment induced surface defects at Ni surfaces [7], no dissociatively chemisorbed CO could be detected on the studied Ni surfaces, as shown in fig. 2a. However, the CO adsorption behavior is drastically changed by alloying Ni with only 9% of Zr. For $\text{Ni}_{91}\text{Zr}_9$, the decrease in molecularly adsorbed CO is accompanied by a corresponding increase in dissociatively adsorbed CO, as shown in fig. 2b (at a temperature of 423 K, $\text{Ni}_{91}\text{Zr}_9$ alloys dissociate CO as effectively as pure Zr).

The strong influence of the Zr atoms on the CO adsorption behavior can be inferred from fig. 3. A hypothetical situation with the dissociation probability of CO strictly proportional to the Zr concentration at the surface would be represented by the dashed line. The observed strong deviation from this behavior (solid line connecting data points in fig. 3) suggests that the promoter effect of Zr is of nonlocal character.

From the experimental data presented here it is evident that the chemisorption of CO on glassy Ni–Zr alloys cannot be interpreted by describing the alloy surface as a mere superposition of Ni-like and Zr-like chemisorption sites. In order to understand the strong influence of Zr on the dissociation behavior, changes in the local electronic structure at the Ni and the Zr sites upon alloying have to be taken into account. Also, while no overall surface segregation of Zr is observed, it seems possible that Zr atoms – due to their larger atomic size – would occupy low coordinated catalytically active “step” sites and thus increase the dissociation probability of CO in a nonlinear way.

In order to understand the electronic origin of the observed catalytic behavior of the investigated systems, we calculated potential energy surfaces

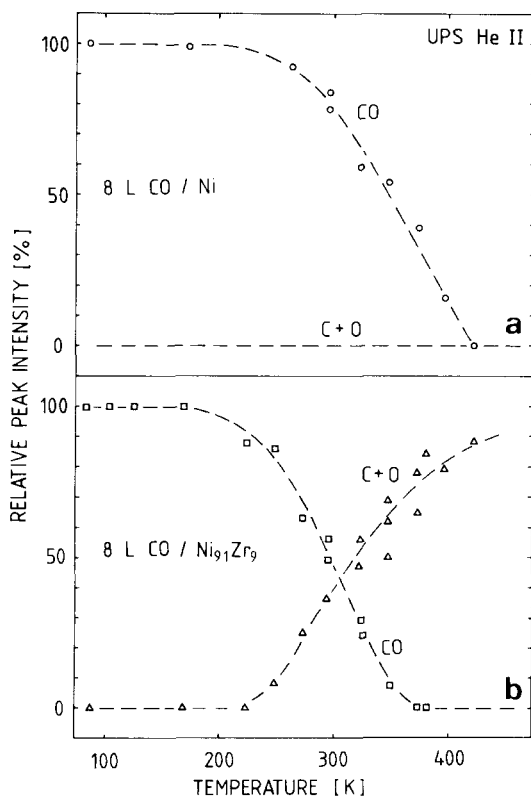


Fig. 2. The amount of molecularly and dissociatively adsorbed CO (100% = maximum observed coverage) as a function of temperature for (a) polycrystalline Ni and (b) the glassy alloy $\text{Ni}_{91}\text{Zr}_9$.

E_{tot} (adsorption geometry) for the CO dissociation at Ni–Zr surfaces. The calculations were performed in the SED (Atom Superposition and Electron Delocalization) formalism described previously [8]. Here the binding energy obtained from a tight-binding Hamiltonian is superimposed by a repulsive term due to Coulomb interactions. This technique has previously been used successfully to determine potential energy surfaces for the CO and N_2 dissociation on various transition metals [9,10] and to discuss the promoting effect of some impurities on the catalytic CO dissociation [9,11]. The parameters used in our calculation are given in table 1.

Since CO adsorbs perpendicularly to Ni surfaces [12], we expect it to break apart across edges or imperfections after a preceding diffusion along the surface in its perpendicular orientation. Here we assume a (111) stepped surface (insert in fig. 4) to be sufficiently represented by a 6-atom cluster (hatched atoms). From our previous calculations it seems that this cluster site

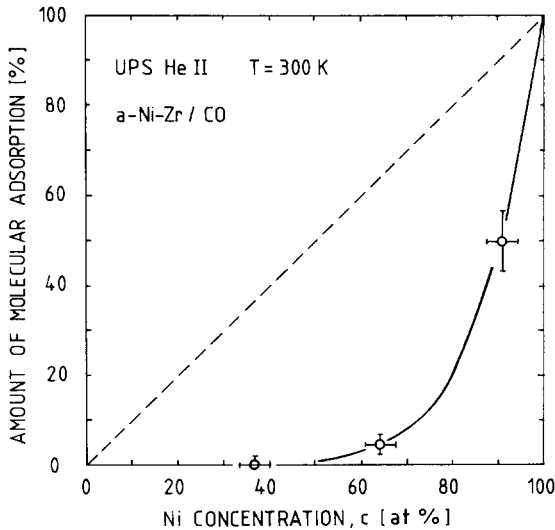


Fig. 3. Amount of dissociatively adsorbed CO on glassy $\text{Ni}_x\text{Zr}_{1-x}$ alloys at $T = 300$ K as a function of substrate composition (solid line). For comparison the expected behavior of a surface which is a mere superposition of Ni and Zr sites is presented (dashed line).

is sufficient to describe correctly relative energy differences. We consider pure Ni surfaces and also substitutional Zr impurities at step sites. The latter case seems to represent correctly dilute Ni–Zr alloys, since a possible moderate tendency of Zr to segregate towards step sites only arises due to its larger atomic size.

In our calculations we restrict the 6 degrees of freedom of the (diatomic) adsorbate to those which are expected to represent the reaction coordinates corresponding to the minimum activation energy for dissociation. In a first

Table 1

Atomic parameters used in the calculation: principal quantum number (n), atomic levels (ϵ) in eV and orbital exponents (ζ); double-zeta Slater basis (with orbital coefficients (C)) has been used for the d levels of Ni

Atom	s			p			d					
	n	ϵ	ζ	n	ϵ	ζ	n	ϵ	ζ_1	ζ_2	C_1	C_2
Ni ^{a)}	4	7.64	1.800	4	3.99	1.500	3	10.00	5.750	2.00	0.568	0.629
Zr	5	6.95	1.817	5	4.93	1.776	4	8.61	3.835	1.505	0.636	0.593
C ^{a)}	2	18.50	1.568	2	9.76	1.618						
O ^{a)}	2	26.98	2.246	2	12.12	2.227						

^{a)} Ref. [9].

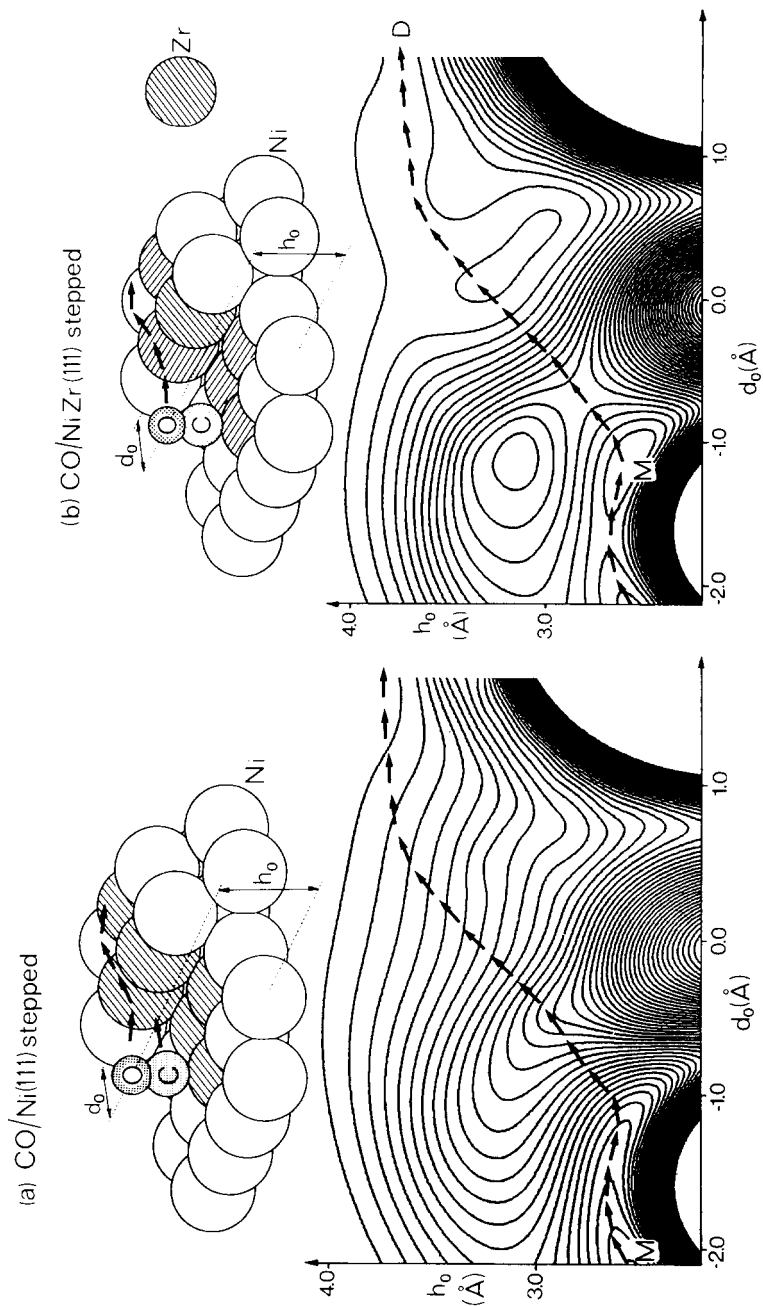


Fig. 4. Potential energy contour plots for the CO dissociation on stepped (a) Ni(111) and (b) Ni–Zr(111) surfaces. h_0 is the height of the O atom above the terrace and d_0 is the respective distance from the step. The C atom is kept fixed during the calculation (note $d_0 < 0$ for terrace sites left from the step). The 6-atom substrate cluster used in the calculation is cross-hatched in the insert. The equidistant contours are separated by 0.2 eV. A possible dissociation path is marked by arrows.

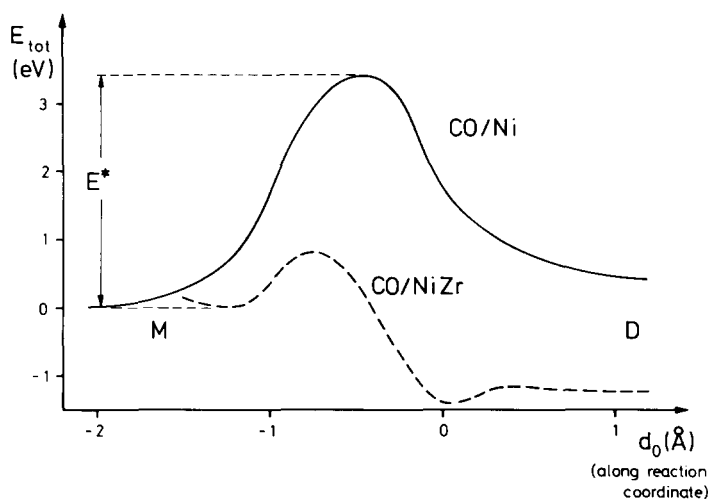


Fig. 5. Potential energy changes (with respect to the molecular state M) for CO dissociation on Ni and Ni–Zr surfaces. The reaction coordinate is assumed along the arrowed path in fig. 4. E^* is the activation energy for dissociation.

calculation the unrelaxed CO ($d_{\text{CO}} = 1.15 \text{ \AA}$) is considered to be perpendicular to the surface, and we vary only the height h_{C} of the C atom above the surface and its horizontal distance d_{C} from the step. After diffusing along the surface, CO will only feel the presence of the step at $d_{\text{C}} \sim 1.6 \text{ \AA}$, where for the relaxed molecule $h_{\text{C}} \sim 1.5 \text{ \AA}$. In a second calculation, shown in fig. 4, we fix the C atom at this position and vary the height h_{O} and the distance d_{O} of the O atom. This describes the tilting and stretching of the CO bond.

Our results for a stepped Ni(111) surface in fig. 4a indicate that CO is first adsorbed in a molecular state (M), with its axis slightly tilted towards the step. In order to dissociate, the O atom will preferentially follow the arrowed path by first surmounting an activation barrier (with respect to M) $E^* \sim 3.4 \text{ eV}$. Similar results for stepped Ni–Zr surfaces are presented in fig. 4b. Fig. 5 shows the total energy during the dissociation and illustrates the strong decrease of the activation barrier for dissociation to 0.8 eV in presence of Zr atoms at step sites. The local minimum at $d_{\text{O}} \approx 0$ in the lower curve in fig. 5 also illustrates the tendency of Zr to form an oxide at step sites. The decrease of the activation energy in presence of Zr explains the strong enhancement of the catalytic activity in Ni–Zr alloys, since the dissociation probability depends exponentially on E^* . As we infer from the analysis of our results, Zr step atoms transfer easily electrons to the nearby CO molecule. Population of adsorbate-localized states of antibonding character weakens the CO bond and thus decreases E^* .

In conclusion, we studied the dissociative adsorption of CO on Ni–Zr

metallic glasses by photoemission and by calculating the potential energy surfaces for a possible dissociation mechanism. From the UPS measurements we obtained information about the amount of dissociated CO as a function of temperature and coverage for different compositions. Chemisorption effects were observed both in the adsorbate and substrate states in the spectra. The experimental findings are supported by microscopic calculations of the CO dissociation at step sites. The inspection of the potential energy surfaces provided an information about the probable dissociation path and the activation energies. The observed strong enhancement of the catalytic activity of Ni by Zr atoms could be explained by the increased backdonation into antibonding CO $2\pi^*$ levels, a typical promotor effect.

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References

- [1] R.D. Kelley and D.W. Goodman in: *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, Vol. 4, Eds. D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1982) pp. 427ff.
- [2] G. Brodén, T.N. Rhodin, G. Brucker, R. Benbow and Z. Hurych, *Surface Sci.* 59 (1976).
- [3] D.L. Cocke and L.H. Yoon, submitted.
- [4] V.L. Moruzi, P. Oelhafen, A.R. Williams, R. Lapka, H.-J. Güntherodt and J. Kübler, *Phys. Rev.* B27 (1983) 2049.
- [5] P. Oelhafen, in: *Topics in Applied Physics*, Vol. 53: *Glassy Metals II*, Eds. H. Beck and H.-J. Güntherodt (Springer, Berlin) ch. 9.
- [6] W. Eberhardt and E.W. Plummer, *Phys. Rev.* B21 (1980) 3245.
- [7] K. Wandelt, J. Hulse and J. Küppers, *Surface Sci.* 104 (1981) 212.
- [8] A.B. Anderson, *J. Chem. Phys.* 62 (1975) 1187.
- [9] D. Tománek and K.H. Bennemann, *Surface Sci.* 127 (1983) L111.
- [10] D. Tománek and K.H. Bennemann, *Phys. Rev.* B31 (1985) 2488.
- [11] N.K. Ray and A.B. Anderson, *Surface Sci.* 125 (1983) 803.
- [12] J.N. Allison and W.A. Goddard III, *Surface Sci.* 115 (1982) 553.