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ADSORPTION OF CO ON HYDROGENATED AMORPHOUS $Ni_{64}Zr_{36}H_{34}$

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Abstract: The influence of hydrogen on the adsorption behaviour of an amorphous alloy has been studied by photoemission spectroscopy (XPS and UPS). On glassy $Ni_{64}Zr_{36}H_{34}$, adsorbed oxygen atoms originating from dissociated carbon monoxide are found to react with hydrogen to form $OH^{\delta-}$ and C_{ads} above room temperature. Adsorption of oxygen, however, leads to a smaller amount of $OH^{\delta-}$ groups at the surface. At 77 K, the formation of water molecules is observed.

In the last few years, surface reactions on metallic glasses have been the subject of many investigations. Basic steps such as CO or oxygen adsorption have often been studied in order to get a fundamental insight into the mechanisms of heterogeneous catalysis [1]. The use of hydrogen containing substrates opens the possibility to observe hydrogenation reactions which are of considerable technological importance, without pretreatment of the surface with hydrogen gas.

Melt spun amorphous alloy ribbons were hydrogenated electrolytically in an acid bath [2] and, prior to the adsorption process, cleaned by means of sputtering with 5 keV Ar ions during 10 min.

Fig. 1a) shows the UPS He II spectra of a $Ni_{64}Zr_{36}H_{34}$ amorphous alloy exposed to 8 L of CO at 77 K at different stages of annealing. At 77 K, the spectrum is dominated by the structures induced by the CO molecules, of which 30 % are already dissociated [1]. The structures at 6, 9 and 12.3 eV binding energy (BE) can be attributed to O $2p$ states of adsorbed oxygen and to $5\sigma/1\pi$ and 4σ orbitals of the CO molecule, respectively. A small peak at 15.4 eV BE can be related to the $1b_2$ valence molecular orbital of adsorbed water [3] indicating that a small amount of oxygen atoms have reacted with hydrogen atoms. Upon warming up the sample, the water molecules desorb, leaving the spectrum of molecular and dissociated CO. Above 270 K, all the CO molecules are either dissociated or desorbed and the UPS spectrum exhibits the typical features of adsorbed oxygen. Further annealing to 400 K causes the growth of a second adsorbate induced peak at 11 eV BE which has been related to the π orbital of the $OH^{\delta-}$ species [4]. The corresponding XPS spectrum of the O $1s$ core level (curve d in fig. 1b) clearly shows the appearance of a shoulder at higher BE of the main line of adsorbed oxygen. The spectrum closely resembles that of a non hydrogenated sample exposed to water at 200 K (curve e of fig 1 b). The shoulder has been attributed to $(OH)_{ads}$ which is a product of the dissociation of water. However, XPS core level spectra of a $Ni_{64}Zr_{36}H_{34}$ sample exposed to 8 L of O_2 at 300 K (curve b) and after subsequent warming to 400 K (curve c) reveals no change of the O $1s$ line shape within the accuracy of the measurement.

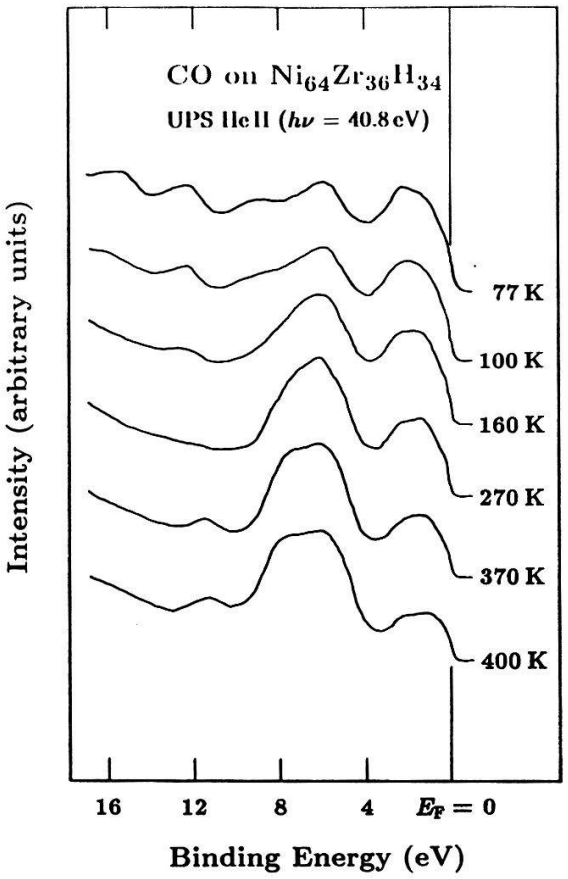

Fig. 1a: UPS He II spectra of $Ni_{64}Zr_{36}H_{34}$ exposed to 8 L CO at 77 K and at different annealing temperatures.

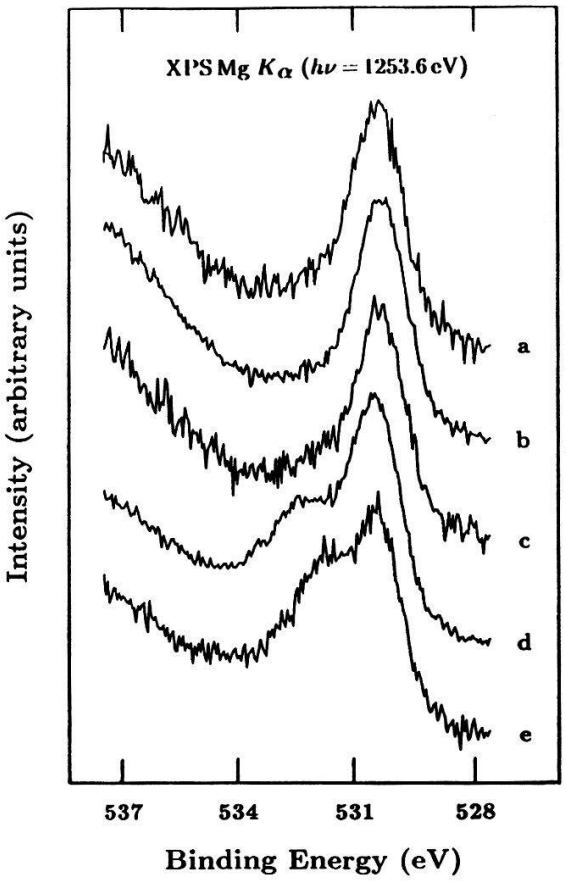

Fig. 1b: XPS O 1*s* core level spectra of a) 8 L $O_2/Ni_{64}Zr_{36}$ at 300 K b) 8 L $O_2/Ni_{64}Zr_{36}H_{34}$ at 300 K c) 8 L $O_2/Ni_{64}Zr_{36}H_{34}$ at 300 K annealed to 400 K d) 8 L $CO/Ni_{64}Zr_{36}H_{34}$ at 77 K annealed to 400 K e) 1 L $H_2O/Ni_{64}Zr_{36}$ at 200 K.

In conclusion, we have shown that a hydrogenated substrate can be used to study surface reactions of adsorbed CO with hydrogen atoms. The hydrogen reacts with oxygen atoms to form either H_2O at low temperatures or $(OH)_{ads}$ at higher temperatures.

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