XPS STUDIES OF THE SURFACE PROPERTIES OF CaNi$_5$

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ABSTRACT

The "air-exposed" sample of CaNi$_5$ contains various oxygenated species on the surface. The surface properties of CaNi$_5$ are analogous to those of LaNi$_5$ with surface enrichment of calcium similar to lanthanum in LaNi$_5$.

INTRODUCTION

Among the intermetallic compounds available for hydrogen storage applications as "rechargeable metal hydrides", AB$_5$ systems have received considerable attention [1]. Because of the capacity to store large amounts of hydrogen, the ease of activation, and the ability to react rapidly and reversibly at ambient temperature and moderate pressures, the alloys LaNi$_5$ and CaNi$_5$ have been studied extensively [2–4]. CaNi$_5$ shows interesting behaviour; it is easily activated at room temperature without requiring any special or preliminary activation treatment such as high-temperature annealing in a vacuum or under a high hydrogen pressure [5, 6].

The surface properties of materials often play critical roles in determining many hydride properties such as the absorption and desorption of hydrogen. The published results on LaNi$_5$ reveal some controversy regarding the nature of the species present on the surface. For example, one group [7–9] has shown an oxygen-induced segregation at the surface with the formation of oxides of lanthanum, together with precipitation of metallic nickel clusters. However, another group [10–12] has reported that both lanthanum and nickel are oxidized at the surface. Moreover, investigations on FeTi, Mg$_2$Ni and Mg$_2$Cu in addition to those on LaNi$_5$ and CaNi$_5$ in this laboratory [13–16] have demonstrated that both of the constituent metals of the alloys become oxidized at the surface, leading to the formation of their respective oxides, albeit of different compositions, upon exposure to air. This has induced us to examine the surface properties of CaNi$_5$, a system analogous to LaNi$_5$.

EXPERIMENTAL

The polycrystalline alloy CaNi$_5$ used in this investigation is a commercial sample obtained from the Ergenics Division of MPD Technology Corporation, NJ, U.S.A., with the designation Hystor-205. The experiments were carried out on the as-received fresh powder samples (unactivated state) under air-exposed conditions at room temperature.

The XPS and XAES measurements were performed using an ESCALAB Mark II instrument (VG Scientific Ltd., UK) equipped with XPS, UPS, AES and argon ion-sputtering facilities. The photoelectrons and Auger transitions are excited with a Mg $K\alpha$ radiation of energy 1253.6 eV and measured with a pass energy of 25 eV. The base pressure of the system was maintained at about 10^{-9} mbar during the analysis. The samples were initially analysed in the as-inserted condition and then subjected to argon ion bombardment at 5×10^{-6} mbar pressure with a beam voltage of 8 kV and a filament current of 60 μA cm^{-2}. The spectra were recorded successively at the end of each sputtering period until all the contamination layers were removed and a steady state was reached. Data were recorded directly using the output of the photon counter on an X–Y recorder at a scan rate of 0.83 eV s^{-1} with a time constant of 0.1 s.

The spectra of the core levels of calcium ($2p$), nickel ($2p$), oxygen ($1s$), carbon ($1s$) and nickel (LMM) Auger transitions were monitored. The spectra were calibrated from the position of the surface carbon ($1s$) photoelectron line resulting from adventitious carbon contaminations contributing to the binding energy value of 284.5 eV and/or with reference to the position of silver metal at 368.2 eV. In most cases it is convenient to use the carbon ($1s$) line for calibration purposes.

RESULTS AND DISCUSSION

Analysis of Ca(2p) spectra

Figure 1 illustrates the XP spectra of Ca($2p$) core levels of CaNi$_5$ before and after sputtering treatments. It is clear from the spectra of the unsputtered sample (at zero time) that the surface is completely contaminated, mostly in non-metallic form. Moreover, the surface calcium concentration relative to nickel is enhanced compared with the bulk composition, a behaviour similar to that of LaNi$_5$. Both nickel and calcium are oxidized at the surface. The chemical state and the binding energy values of the various species are given in Table 1.

It should be noted that on the fresh surface, hydroxide and carbonate species are formed in addition to the oxide species. This is indicated by the appearance of high binding energy bands (see Fig. 1 at zero time). In addition, clear evidence for the presence of CaCO$_3$ and Ca(OH)$_2$ is obtained from the binding energy values of C($1s$) and O($1s$) core levels [17].
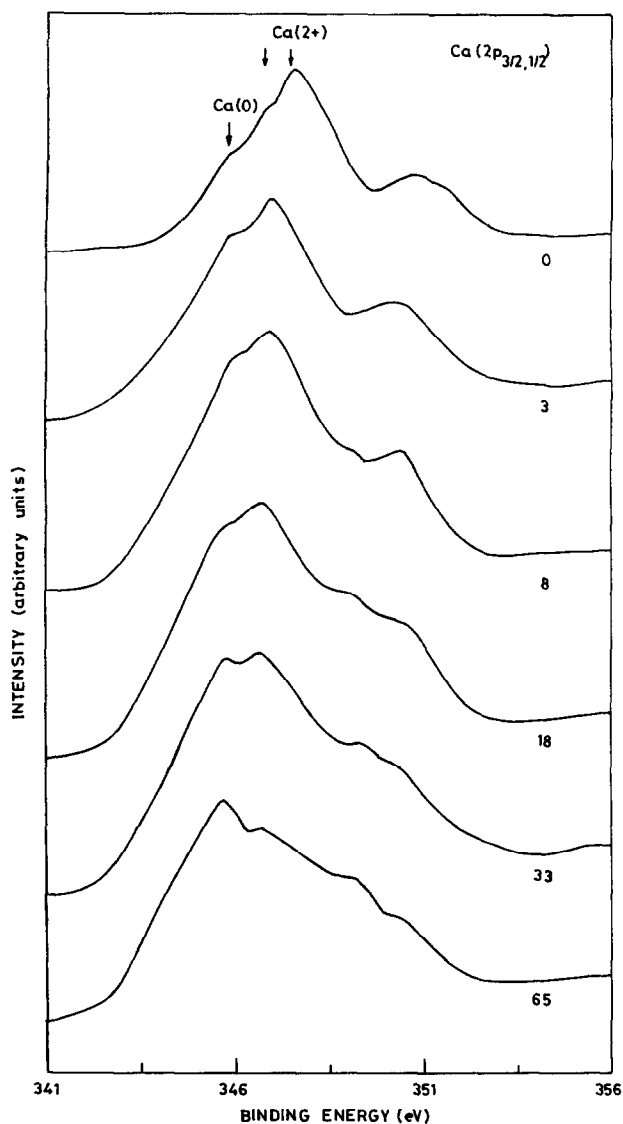
Fig. 1. XPS of Ca(2p) core levels of fresh CaNi$_5$ (air-exposed) before and after sputtering (time in minutes).

Even though this study describes only surface oxides and hydroxides, it should be realized that an oxidative process in air produces other species, particularly carbonates, on all the alloys studied, e.g. LaNi$_5$, CaNi$_5$, FeTi, Mg$_2$Ni and Mg$_2$Cu [14, 17]. In general, non-oxide and/or hydroxide species are present on the

TABLE 1

XPS data for the Ca($2p$) core levels of fresh CaNi$_5$ alloy*

Surface state	Surface species	Binding energy (eV)	
		$2p_{3/2}$ region	$2p_{1/2}$ region
Air-exposed	Ca(OH)$_2$	347.6[a]	351.5[a]
	CaCO$_3$[b]		
	CaO	347.0	350.6
Sputtered	Ca	345.7	349.3
(>1 hr)	CaO$_{ads}$[c]	347.2	350.8

*Values are deduced from Fig. 1.
[a]This could be due to the contribution from both Ca(OH)$_2$ and CaCO$_3$ species.
[b]This species has been assigned based on the spectra of C($1s$) and O($1s$) regions. In this case, the carbonate species probably dominates (as evidenced from C($1s$) spectra) rather than the hydroxyl species [17], unlike in LaNi$_5$ where the hydroxyl species predominates [16].
[c]This is considered as an adsorbed species.

outer passivated surface only in small amounts. However, a pronounced increase in carbonate species is noticed in the case of CaNi$_5$ compared with the other systems [17]. The presence of oxides and hydroxides of both calcium and nickel and the additional carbonate species, which also predominates in this case, on the surface of CaNi$_5$ contribute to the broadening of the O($1s$) region, which in turn complicates the analysis.

It should be noted that the appearance of calcium metal is noticed even in the unsputtered samples. This suggests that the calcium is oxidized only to a few layers depth. The CaO layer thickness formed on CaNi$_5$ is definitely less than that of La$_2$O$_3$ formed on LaNi$_5$. Upon sputtering, the carbonate and hydroxide species are completely removed and only the oxide layers are apparent, as can be seen from Fig. 1 and from the binding energy values given in Table 1. The $2p$ separation values of about 3.4 eV indicate the presence of calcium in the oxidized form, which is in agreement with the results reported from this laboratory [18] and for pure CaO [19]. It is also seen from Fig. 1 that the appearance of metallic calcium occurs at the early stages of sputtering. However, complete disappearance of the signals due to CaO is not obtained. This could be due to the formation of protective carbide layers [20], which are difficult to sputter.

Analysis of the Ni(2p) spectra

The XP spectra of the Ni($2p$) region for the air-exposed and subsequently sputtered CaNi$_5$ sample are shown in Fig. 2. The resulting $2p$ spectra of the fresh sample (at zero sputtering time) are identical with the spectra of bulk and/or surface NiO or pure nickel exposed to air [21–26], thus identifying the surface reaction product. The binding energy values for the different species
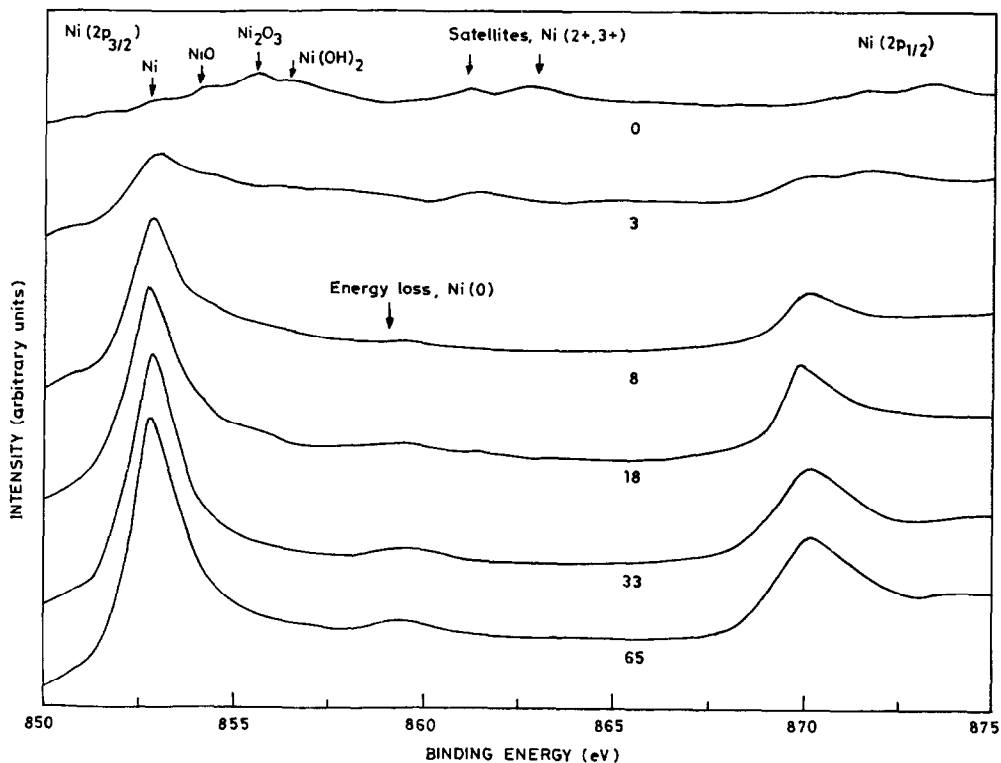
Fig. 2. XPS of Ni(2p) region of fresh CaNi$_5$ (air-exposed) before and after sputtering (time in minutes).

of CaNi$_5$ are given in Table 2. The appearance of peaks at about 1.7, 2.7 and 3.7 eV away from the metal core level indicate the existence of different nickel species. Based on the binding energy values of the metal core level as well as the ligand core level, the species are identified as NiO, Ni(OH)$_2$ and Ni$_2$O$_3$.

The identification of Ni$_2$O$_3$ is slightly difficult in most cases because NiO also exhibits a band at 855.8 eV [21, 24]. However, in the present instance the intensity of the 855.8 eV peak is higher than that for NiO and that of the 854.6 eV peak itself, thus suggesting that this contribution could be from the Ni$_2$O$_3$ species. It should be mentioned that NiO exhibits a feature at 855.8 eV of lower intensity than that at 854.6 eV [21, 24]. The results are further supported by the analysis of the satellite structures. The binding energy values for the satellites are also given in Table 2. The appearance of satellite features at 861.5 and 862.7 eV indicate the presence of nickel as NiO and Ni(OH)$_2$. However, the latter shows a broad and more intense band. This could be due to the co-existence of Ni$_2$O$_3$ satellite with Ni(OH)$_2$ satellite.

TABLE 2

XPS data for the Ni$(2p_{3/2})$ core levels of fresh CaNi$_5$ alloy*

Surface state	Surface species	Binding energy (eV)
Air-exposed	NiO[a]	854.3
		861.5[b]
	Ni$_2$O$_3$	855.5
		862.7[c]
	Ni(OH)$_2$	856.5
		862.7[c]
Sputtered	Ni	852.8
(>1 hr)		858.4[d]

*Values are deduced from Fig. 2.
[a]The high binding peak (855.8 eV) normally associated with NiO probably overlaps with that of Ni$_2$O$_3$ (855.5 eV). It should be noted that in the case of NiO the relative intensity of the peak at 854.3 is greater than that of the peak at 855.8, whereas in the present case it is less. Hence, this indicates the presence of Ni$_2$O$_3$.
[b]Monopole charge transfer satellites (shake-up) characteristic of NiO.
[c]Broad lines (Shake-up nature) may be due to the overlap of Ni$_2$O$_3$ and Ni(OH)$_2$. However, this is characteristic of the species.
[d]Energy loss/shake-up feature characteristic of Ni in the metallic state.

Analysis of Ni (LMM) Auger transitions

Figure 3 shows the XAE spectra of the passivated and surface-cleaned CaNi$_5$ alloy. The spectrum of the unsputtered sample clearly shows the passivated or contaminated nature of nickel. The presence of different species has been identified from the kinetic energy values and is presented in Table 3. The various surface species are easily differentiated, unlike the Ni(2p) spectra. However, upon sputtering the oxide layers are depleted and the appearance of sharp peaks indicates that nickel is in the metallic state. The observed values for the various species are in agreement with the published values for nickel–oxygen systems [25], suggesting that oxidation takes place in a similar fashion. It should be noted that even after the first sputtering, a small amount of the NiO species exists, as can be seen from Fig. 3, and the corresponding binding energy values indicate that most of the oxidized nickel is present as NiO.

Weaver and coworkers [11, 12] have also observed, from their UPS measurements, the oxidized nature of nickel in the first few monolayers of the oxygen-exposed Haucke compounds (LaNi$_5$, CaNi$_5$, YNi$_5$ and ThNi$_5$), although lanthanum, calcium, yttrium and thorium oxidize quite rapidly. Even though the results are in agreement with our results, we feel that the analysis using the structure of the valence band measurements in binary systems is
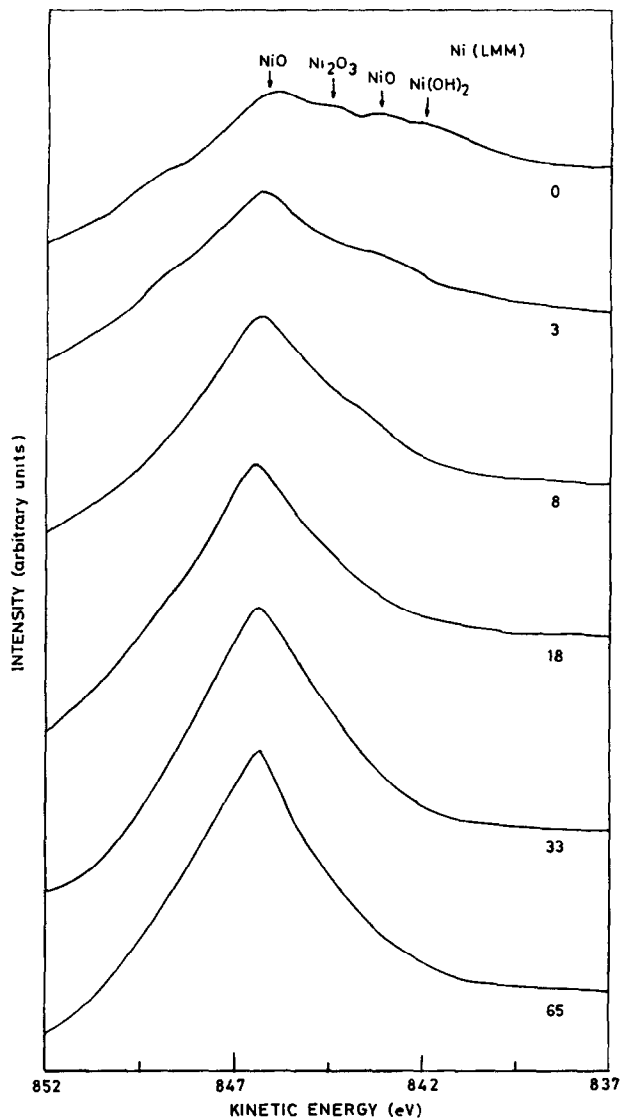
Fig. 3. XAES of fresh $CaNi_5$ (air-exposed) before and after sputtering (time in minutes).

rather difficult because of the overlap of the bands of the constituent elements. Schlapbach [9] has also pointed this out clearly earlier. Shamir et al. [27] have reported the oxidized nature of nickel on the europium-substituted $CaNi_5$ alloys from XPS and UPS measurements.

In the present study also calcium was oxidized to CaO on $CaNi_5$, but in the presence of water vapour and carbon dioxide (possibly from the atmosphere) it gave $Ca(OH)_2$ and $CaCO_3$, respectively. It is interesting to note that an

TABLE 3

XAES data for the Ni (*LMM*) Auger transitions of CaNi$_5$ alloys*

Surface state	Surface species	Kinetic energy (eV)
Air-exposed	NiO[a]	846.0
		843.2
	Ni$_2$O$_3$[a]	844.4
	Ni(OH)$_2$[a]	842.0
Sputtered (> 1 hr)	Ni[b]	846.3

*Values are deduced from Fig. 3.
[a]Broad features characteristic of the oxidized nature of the Ni species (see also text).
[b]Sharp peaks characteristic of metallic Ni.

increase in carbonate species is observed in this case [17]. However, the presence of different oxygenated species of nickel (NiO, Ni(OH)$_2$ and Ni$_2$O$_3$) could be explained on the basis that upon exposure of the alloy to air, results in the formation of CaO. As these oxides are formed, nickel is squeezed out (it should be noted here that the alloy is nickel-rich) and the aggregates in some cases intersect the surface, where they bind with excess oxygen and hence produce mainly a mixture of oxidized products in the case of CaNi$_5$ as also in LaNi$_5$ [16].

Although oxygen is capable of penetrating and forming oxides at least several atomic layers below the surface, the formation of surface hydroxides, carbonates and/or the terminal oxides in the present case may prevent further reaction, thereby decreasing the segregation of the components in these alloys. It is worthwhile to mention here that the lanthanum-to-nickel ratio on LaNi$_5$ is about 1:1 on the oxidized surface [9, 28]. The calcium-to-nickel ratio in CaNi$_5$ is slightly less (more surface nickel is observed) than in LaNi$_5$.

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