Letter

The influence of atmospheric CO_2 on the surface properties of Mg_2NiH_4 and a comparison with some hydrogen storage alloys

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Recently, we reported [1–6] on the surface properties of various compounds of the type, AB, AB_5, A_2B and A_2BH_4 (A ≡ Mg, Ca, Ti or La; B ≡ Fe, Ni or Cu). Special attention was given to the oxidation states of the different elements. It was shown that the air-exposed samples result in the formation of surface oxides and hydroxides on all the studied alloys and hydrides. This has been related to the surface deactivation or a periodic activation requirement of the alloys. A new approach [7, 8] to the activation mechanism has been attempted and suggested a supported-metal-type species, upon activation, is responsible for the initial reaction with hydrogen. Despite some promising results, a number of other interesting and impressive observations, such as the formation of higher valency terminal oxides [3, 4, 6], lower valency suboxides [1, 5], ion-induced carbides [9] and carbonates [10] created significant interest. In this respect, we extend our previous work [10] on the interaction of atmospheric CO_2 on intermetallic compounds and show that a new carbonate species, not reported so far, exists at the surface of Mg_2NiH_4. It was also noticed that the oxidation behaviour of the hydride is quite different from the alloys.

The study of the surface properties of hydrogen storage materials has received much attention in view of the development of activation procedures in connection with the hydriding and dehydriding processes. Gaseous impurities, such as O_2, H_2O, CO, CO_2, SO_2, H_2S etc., are well-known catalytic poisons to pure and/or oxidized metallic/alloy surfaces [11]. As a consequence, the surface is readily passivated, resulting in the formation of numerous oxidic and hydroxidic species. However, it has been thought that the interaction of atmospheric gases other than O_2 and moisture is generally small, owing to their relatively lower concentrations, and hence it has been overlooked in most cases [12]. Unfortunately, the concentrations of such species on the outer surface on well-studied systems are rather low which sometimes prevents their identification. Since the atmosphere

contains significant amounts of CO_2 and in presence of O_2 and/or moisture or at the oxidized surface, it is expected to interact, since many metal oxides and hydroxides have been shown to adsorb CO_2 readily at room temperature [13]. That is, they seem to have a special reactivity towards the activation of CO_2. Parenthetically, the subject of CO_2 adsorption is of considerable importance from a fundamental and applied point of view. For example, with respect to hydrocarbon and methanol syntheses from $CO-CO_2-H_2$ mixtures [14], the water gas shift reaction [15] and solar energy conversion by the photocatalytic reduction of CO_2 [16].

The hydride, Mg_2NiH_4 and the alloys, Mg_2Ni, Mg_2Cu, $LaNi_5$, $CaNi_5$ and TiFe were the same samples used in our earlier investigations [1–6]. The experimental conditions, techniques, procedures and the analysis have been discussed in detail elsewhere [4, 7, 10, 17]. In the present study, we report on X-ray photoelectron spectroscopy (XPS) analytical results for the C(1s) region. All the measurements were carried out on the air-exposed samples at room temperature. The recorded spectra consist of two or more peaks, the dominant being the hydrocarbon line (spectrometer chamber contamination; see signals marked as 1 in Figs. 1 and 2) at
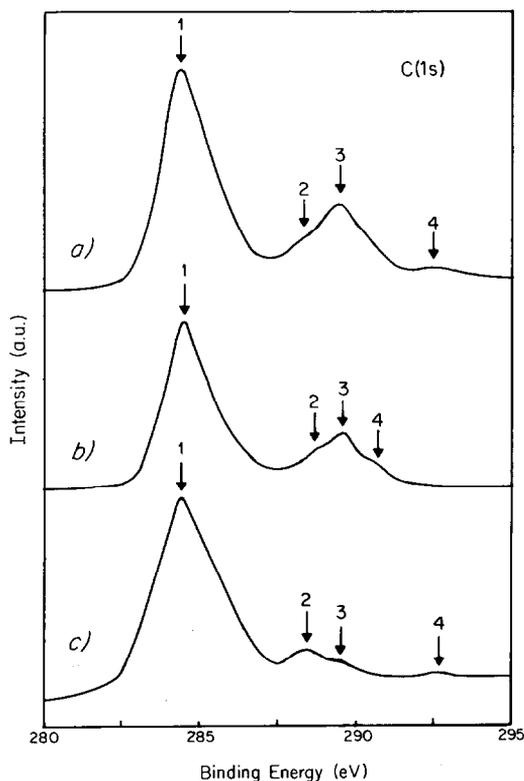
Fig. 1. XP spectra of air-exposed samples of (a) Mg_2Ni, (b) Mg_2Cu and (c) Mg_2NiH_4. The numbers represent the nature of different signals: 1, indicates reference carbon; 2, 3 and 4 imply CO_2 adsorbed on different sites (see text).
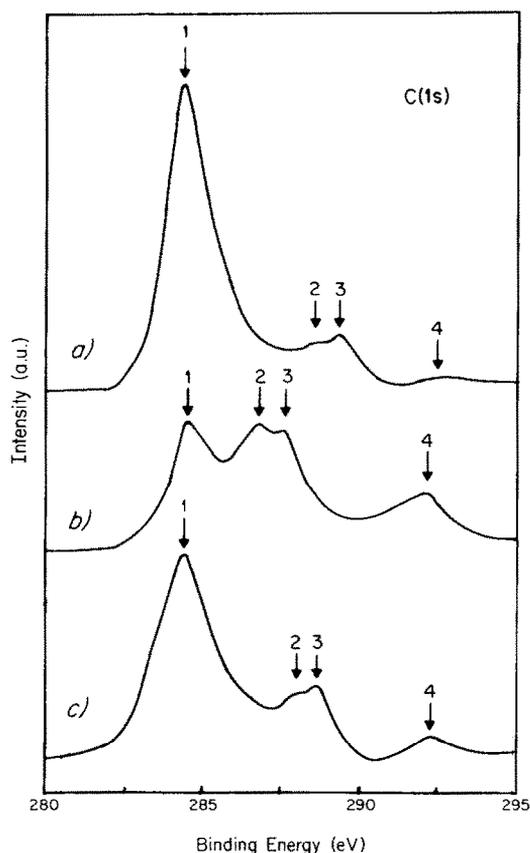
Fig. 2. XP spectra of air-exposed samples of (a) $LaNi_5$; (b) $CaNi_5$ and (c) TiFe. The peak numbers carry the same assignments as described in Fig. 1.

lower binding energy and the others at higher binding energy may be originating from chemisorbed and physisorbed CO_2 on the various sites generated at the surface, since carbon is known to appear at different binding energies when it is attached to chemically different atoms or groups [18]. Unlike the pure/individual components, the collective presence of various oxides and hydroxides as well as the additional carbonate species contribute to the broadening of the $O(1s)$ peaks (mainly of more than one oxygen environment around the metal atoms) and hence complicate the analysis. In addition, the relatively lower concentration of the carbonates, in most cases, prevents a clear identification. Hence, on the basis of $O(1s)$ signals alone it is rather difficult to recognize the various species. Therefore, the $C(1s)$ region has been adopted for this purpose and is quite useful in this regard. It is noteworthy that $CaNi_5$, however, shows a clear indication of the carbonate species even in the $O(1s)$ region [19]. The high intensity of the peaks are in accordance with the $C(1s)$ results.

Figure 1 shows the typical $C(1s)$ spectra of Mg_2Ni, Mg_2Cu and Mg_2NiH_4. As stated earlier, the high intensity low energy signals are due to the reference carbon

(284.5 eV) and the low intensity high energy peaks can be due to carbon atoms in non-equivalent positions, namely the adsorption of CO_2 in different modes [10]. The multiple peaks in the range 288.5–289.5 eV (peaks indicated as 2 and 3) can be attributed to the chemisorbed CO_2 species on the different sites available for bonding and are assigned respectively, for example in the case of Mg_2NiH_4, Mg_2Ni and Mg_2Cu, to anhydrous and basic carbonates of magnesium. The weak features at high binding energies 290.5–292.5 eV (peaks marked as 4), can be due to a weak bond between the adsorbent and the adsorbate. They can also be designated to the carbonate-type species of nickel and copper respectively on Mg_2NiH_4/ Mg_2Ni and Mg_2Cu. The results are further supported by the characteristic carbonate signals in the O(1s) region at 533.5–534.5 eV [19]. A similar observation has also been noticed on other systems, such as $LaNi_5$, $CaNi_5$ and TiFe (see Fig. 2 and ref. 10) and the same explanation also holds good for these alloys. The exact peak positions and the assignments of various species are summarized in Table 1

TABLE 1

XPS data for the surface carbonates on various systems from the C(1s) region

Compound	Binding energy (eV) and assignment		
	Carbonate[a]	Bicarbonate[a]	Adsorbed CO_2[b]
Mg_2NiH_4	288.4[c]	289.5	~292.5[d]
Mg_2Ni	288.5	289.5[c]	~292.5[d]
Mg_2Cu	288.6	289.5[c]	~290.5
TiFe	288.0	288.9[c]	292.4
$CaNi_5$[e]	286.8[c]	287.7[c]	292.2
$LaNi_5$	288.6	289.3[c]	~292.5[d]

[a]On the oxidized surface of magnesium, calcium, titanium or lanthanum.
[b]On the oxidized surface of iron, nickel or copper.
[c]Major components.
[d]Weak and broad signals.
[e]Also shows distinct features in the O(1s) region corresponding to a binding energy values of 533.1 and 534.0 eV respectively for anhydrous and basic carbonates [19].

and the values are in excellent agreement with literature reports [18, 20]. They are typical for strongly and weakly bonded CO_2 molecules on the metal oxides/ oxidized metals (surface carbonates) or the bulk carbonates themselves, though the latter give features that are slightly shifted to lower binding energies. The apparent order of CO_2 adsorption on these materials is as follows:

$$CaNi_5 > Mg_2Ni > Mg_2Cu \geqslant TiFe > LaNi_5 \geqslant Mg_2NiH_4 \qquad (1)$$
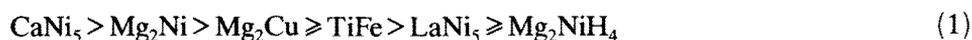
However, the relative amounts of the different species depend upon the chemical reactivity of the elements towards various gas molecules.

It has been noticed that the magnesium-based hydrides exposed to air show an increase in the desorption temperature [17] and this is consistent with the report of

Ono *et al.* [21], who have also observed a deactivation of the hydrides when treated with air or CO_2. This could be related to the interaction of H_2O and/or CO_2 at the surface. A number of publications described the adsorption of H_2O and CO_2 on metal oxides, such as MgO, CaO, TiO_2 and La_2O_3 [13, 20]. In general H_2O and CO_2 can be chemisorbed to form surface hydroxides and carbonate respectively. In fact, it has been suggested that in the presence of moisture, bicarbonate species predominate and the present results are in close agreement with this observation. However, for hydrided samples carbonate species seem to be favoured rather than basic carbonates (see Fig. 1 and Table 1). This unusual behaviour can be explained, based on the reactivity of hydrides towards the atmospheric gases. Since most of the hydrides will react with moist air to a greater extent to form the oxides and to a lesser extent to form hydroxides. Hence, it is expected to behave quite differently compared with the metals/alloys. H_2O vapour attacks the hydrides much more vigorously than either O_2 or CO_2. However, the degree of reactivity depends on the nature of the hydride.

Unfortunately, precise surface analysis data are not available for the air-exposed hydride systems owing to the complications arising from stability factors and lack of interest in the past. It is known that the hydrides are stable towards pure O_2; however, they decompose in the presence of moist air or H_2O. For example, the alkaline earth metal hydrides, such as MgH_2 (since the binary hydrides have a simpler chemistry and let us consider them here for the sake of discussion) dissociate in humid air in the following way:

$$MgH_2 + H_2O \longrightarrow MgO + 2H_2 \qquad (2)$$

Since moisture is preferentially utilized for this reaction, CO_2 interacts with the oxidized surface with ease; thus forming, mostly, anhydrous carbonates. A similar hypothesis can be extended to Mg_2NiH_4 as the chemistry involved is the same in both cases

$$Mg_2NiH_4 + 2H_2O \longrightarrow 2MgO + Ni + 4H_2 \qquad (3)$$

Whereas in the case of the metal/alloy surface, the initial reaction takes place with O_2 itself and therefore competition between H_2O vapour and CO_2 results for a further reaction. Since H_2O vapour is known to have a stronger effect than CO_2, at first, it produces hydroxides. Subsequently, CO_2 reacts with this surface and results, mainly in basic carbonates. The considerable amounts of carbonate species observed on magnesium- and calcium-containing alloys (see Figs. 1 and 2) could be due to the fact that the alkaline earth oxides have (in addition to their segregation and oxidation behaviours) a large surface area and a high reactivity towards CO_2 and thereby facilitating the adsorption to a greater extent. Among the magnesium- and calcium-based samples, the relatively large amounts of carbonates on $CaNi_5$ could be understandable based on the sorption behaviour of CO_2 on MgO and CaO, where the latter is known to possess a high affinity under given conditions [13].

Interestingly, the conditions of humidity and atmospheric CO_2 tend to have fairly substantial effects on the outer surface chemistry. The distinction between these carbonates and the other species, namely the different oxides and hydrox-

ides, reveals a surface heterogeneity. It is also expected that the roughness or defects (the ill-defined non-stoichiometry results as a matter of partial oxidation) on the oxide surfaces play important roles in adsorption. Reproducible and reliable results on the individual alloy, hydride systems have made it possible to identify the newly observed carbonate species. Oxidation in air seems to differ from that in pure O_2 largely because of the active part played by the H_2O vapour. Accordingly, on the outer surface, $LaNi_5$ [3, 6], Mg_2Ni [2, 3, 5], Mg_2Cu [3, 5] and Mg_2NiH_4 [2] show large amounts of hydroxyl species and carbonates seem to be predominant in the case of $CaNi_5$ [4, 10] whereas the alloy TiFe [1] indicates a distribution of both oxides and hydroxides nearly equally. Upon sputtering for short periods, the oxides dominate in all the cases. It is worth mentioning that the O_2-exposed samples of TiFe show signals only due to the oxides [7, 19].

Based on the above results and from our earlier work, we propose the following possible reaction mechanism that is expected to occur commonly at the surface of the alloys and hydrides upon exposure to air:

$$(\text{Metal}) + O_2 \longrightarrow O^{2-} \tag{4}$$

$$(\text{Hydride}) + H_2O \longrightarrow O^{2-} \tag{5}$$

$$O^{2-} + H_2O \longrightarrow 2OH^- \tag{6}$$

$$O^{2-} + CO_2 \longrightarrow CO_3^{2-} \tag{7}$$

$$OH^- + CO_2 \longrightarrow HCO_3^- \tag{8}$$

That is, after an initial oxidation of the surface (step (5)), reaction (7) predominates in the case of a hydrided sample, whereas on the metal/alloy surface, after the first stage of oxidation (step (4)), reactions (6) and (8) prevail, depending upon the reactivity of the individual systems [1–6]. It is noteworthy that anhydrous CO_2 is compatible with commonly used metals and alloys at normal temperatures but moist air is corrosive.

Thus it is believed that the passivated layers on the outer surface, in most cases, protect the materials by preventing them from further degradation. That is, it is expected that the surface hydroxides and carbonates as well as the oxides play an important role in the material durability, since a further reaction with O_2 and/or other gaseous impurities may be hindered by low sticking probability. We have attempted to point out a common feature which is unnoticed at the surface of the alloys and hydrides. The results may open up new possibilities for identification and therefore a clear understanding of the various surface reactions. The most significant feature of these materials is that surface chemistry plays a crucial role in determining the activation and deactivation processes. However, an overall picture of the surface properties, activation and deactivation mechanisms, reactivity and other subjects related to this topic, such as surface segregation, oxidation etc., will be summarized in a follow-up report [19].

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