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EVIDENCE FOR THE FORMATION OF SURFACE CARBONATES ON SOME HYDROGEN STORAGE INTERMETALLIC COMPOUNDS: AN XPS STUDY

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Abstract—X-Ray photoelectron spectroscopic (XPS) studies of air exposed samples of $LaNi_5$, $CaNi_5$, Mg_2Ni, Mg_2Cu and FeTi indicate that the interaction of atmospheric carbon dioxide results in the formation of surface carbonates in addition to the usual oxides and hydroxides. The reaction of carbon dioxide, in fact, is favoured by the oxidized surface which in turn produces the carbonate species on the top few layers, hitherto not reported. In particular, the carbonates seem to be predominant in the case of $CaNi_5$. The adsorption of carbon dioxide also gives an idea of the segregated elements of the different systems. Even though such carbonate species on the alloy surfaces seem to be expected rather than surprising, there is no evidence available in the literature. To our knowledge, this forms the first report on such a problem. The results also provide valuable information concerning the understanding of various surface reactions and the nature of activation processes which often differ between materials involved in hydrogen uptake.

INTRODUCTION

It is known that surface oxides and hydroxides are formed on the intermetallic compounds upon exposure to air [1–4]. Chemisorption and initial oxidation of metal, alloy, and intermetallic surfaces are important to the basic understanding of different phenomena such as, corrosion, catalysis, thin film technology and other related fields. Therefore, identification of such surface species is of prime importance in elaborating the mechanism of catalytic reactions on solid surfaces. The study of surface properties of hydrogen storage intermetallics has received considerable attention in view of the development of activation procedures as well as to improve the hydriding properties of these systems with commercial sources of hydrogen—like hydrogen from steam reforming of hydrocarbons, which are known to contain contaminants, namely, oxygen, moisture and carbon dioxide. The presence of various types of oxide and hydroxide species on the surfaces of these alloys seem to have special reactivity towards the activation of carbon dioxide. Incidently, the study of activation of carbon dioxide on these surfaces has relevance from the point of view of the synthesis of methanol at low temperatures on supported metal systems [5, 6].

Since the atmosphere contains significant amounts of carbon dioxide [7], it can also be expected to influence the degradation of the materials in a similar way to that observed with oxygen and moisture. However, the interaction of carbon dioxide will take place only after the initial oxidation of the metallic surface by oxygen or water vapour or both, since the latter reactions are thermodynamically more favourable than the former. Carbon dioxide, however, is less chemically aggressive than either oxygen or moisture and, moreover, it is inert towards pure metals.

In the earlier studies [8, 9], it has been thought that the amount of non-oxide and/or non-hydroxide species formed on the outer surface of various metals and alloys is probably small and hence has been neglected. Even though the formation of a carbonate is not unexpected, until today, to our knowledge, there is no data available of the presence of such species. On the other hand, the easy activation of the alloy, $CaNi_5$, compared to many other well known systems has been related to the influence of atmospheric carbon dioxide [10] in addition to its segregation behaviour [11]. Its effect at ambient conditions can be restricted to sub-monolayer chemisorption (in most cases) and as a result, carbon dioxide can be a good probe for discriminating between different surface states. It was this situation which stimulated the present investigation.

However, the problem of identification of adsorbates in monolayer amounts arises frequently in surface studies. Though there are numerous techniques which provide data on such phenomena, XPS is one of the few methods which has potential for providing details of the nature of complex adsorbed species. Thus, our effort here involves the application of XPS for the characterization of the adsorbed carbon dioxide. We also show a new carbonate species, not reported so far, which is formed on different alloy surfaces upon exposure to the atmosphere.

EXPERIMENTAL

The detail of the samples ($LaNi_5$, $CaNi_5$, Mg_2Ni, Mg_2Cu and FeTi) used, the experimental techniques employed and the procedures involved in the present study are given elsewhere [12–14]. Carbon (1*s*) and oxygen (1*s*) XPS lines have been mainly used to identify the nature of adsorbed carbon dioxide molecules (either chemisorbed or physisorbed or both types) on the surface. The peak positions were assigned by setting the carbon (1*s*) contamination signal to a binding energy value of 284.5 eV and the $3d_{5/2}$-level of silver metal at 368.2 eV. In order to check if the high binding energy peaks in the carbon (1*s*) region are only due to the reaction of atmospheric carbon dioxide, sputtered (by argon ion bombardment) samples were exposed to pure oxygen in the reaction chamber itself. The resulting spectra showed a signal corresponding to the adventious carbon and do not give any additional features. As expected this signal appears, however, only on long standing.

RESULTS AND DISCUSSION

Figure 1 shows typical XP spectra of the carbon (1*s*) region for the air exposed samples of $LaNi_5$ and $CaNi_5$ intermetallics. The dominant feature at 284.5 eV (used as reference; peaks marked as 1) is due to background carbon arising out of the contamination from the spectrometer which is confirmed by its growth with time on the sputtered samples. The higher binding energy emissions, in the region of 286.5–289.5 eV (peaks marked as 2 and 3) and 291.0–293.0 eV (peaks marked as 4), could have arisen from the interaction of the surface with atmospheric carbon dioxide, after an initial reaction with oxygen and moisture. That is, a carbonate type species could be responsible for the shifts in the binding energies. It should, however, be noted that such large shifts in the carbon (1*s*) region have been observed for several carbon-containing compounds [15, 16].

The presence of various oxides and hydroxides of the segregated elements of the alloys and the additional carbonate species on the surface constitute the broadening of the peaks in the oxygen (1*s*) region. The appearance of high binding energy signals (533.0–535.0 eV; [11]) indicate a different nature of oxygen species than the normal low energy features due to oxides and hydroxides. Tentatively, one can assign these emissions to carboxyl type species. Hence, the high energy features in the carbon (1*s*) region could be attributed to the adsorption carbon dioxide on various types of sites available for bonding. The observed binding energy values are typical of strongly and weakly bonded carbon dioxide on pure binary metal oxide and oxidized metal surfaces [17–21]. Among the high energy emissions, the signals at 286.5–289.5 eV (Fig. 1; peaks marked as 2 and 3) are assigned to the formation of carbonates (both anhydrous and basic) of lanthanum (Fig. 1a) and calcium (Fig. 1b). Supporting evidence for this observation has been noticed from the oxygen (1*s*) signals at 533.0–535.0 eV (see [11]), typical of carbonate type moities. In Fig. 1, the signals at 291.0–293.0 eV (peaks marked as 4) could be attributed to weakly adsorbed carbon dioxide on the oxidized surface of both $LaNi_5$ and $CaNi_5$, possibly on nickel sites, as the case with the adsorption of carbon dioxide on nickel oxide [17, 21].

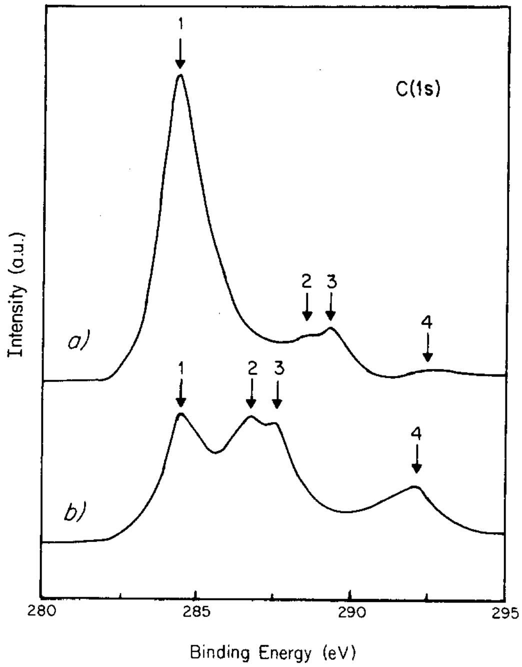

Fig. 1. XP spectra of air exposed samples of: (a) $LaNi_5$ and (b) $CaNi_5$. The numbers represent the nature of different signals: 1–reference carbon; 2–, 3– and 4–carbon dioxide adsorbed on different sites (see text).

Similar carbon (1*s*) spectra were also obtained for the air exposed samples of Mg_2Ni and Mg_2Cu. Typical spectra showing such behaviour is illustrated in Fig. 2. The resulting spectra suggest that an identical reaction mechanism to that of $LaNi_5$ and $CaNi_5$ (see Fig. 1), would have taken place in these materials also upon the exposure of the virgin alloys to atmosphere. Accordingly, carbonate species of magnesium, nickel, and copper are formed on the surface. The different peaks in the region 288.5–289.5 eV (Fig. 2; peaks marked as 2 and 3) are due to the existence of anhydrous and basic carbonates of magnesium. On the other hand, the high binding energy features (Fig. 2; peaks marked as 4) could be attributed to the adsorbed carbon dioxide molecules on the initially oxidized surfaces of nickel (Fig. 2a; peak 4;

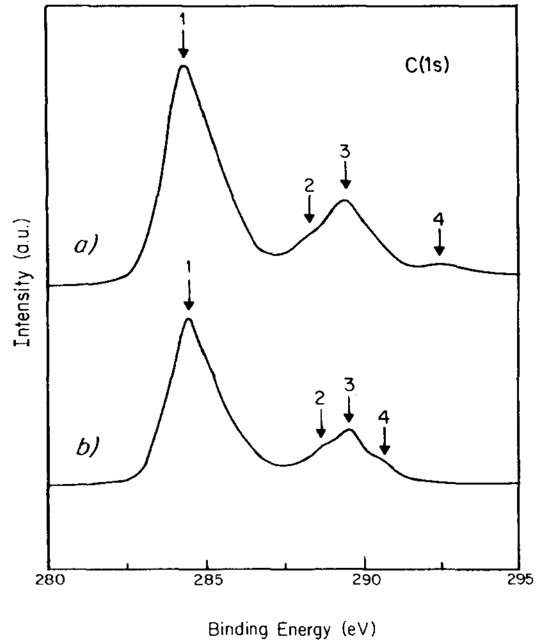

Fig. 2. XP spectra of air exposed samples: (a) Mg_2Ni and (b) Mg_2Cu. The peak numbers carries the same assignments as described in Fig. 1.

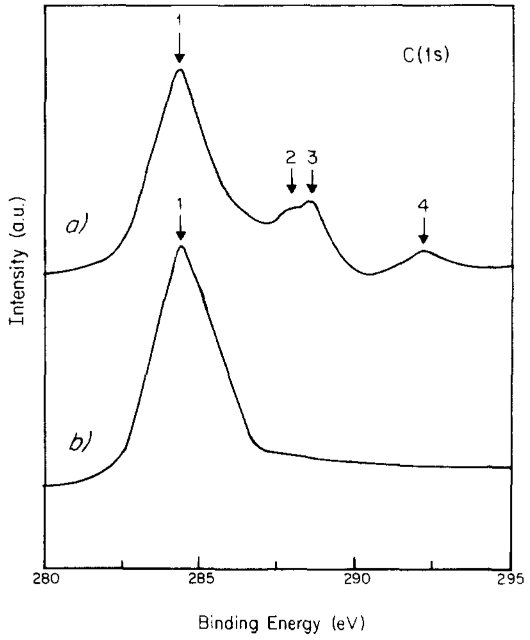

Fig. 3. XP spectra of FeTi alloy under different experimental conditions: (a) air exposed and (b) oxygen exposed. The peak numbers represent the same assignments as described in Fig. 1.

292.5 eV), and copper (Fig. 2b; peak 4; 290.5 eV) as the case with post-transition metals [17–21]. The oxygen signals in the (1*s*) region at 533.0–535.0 eV also supports the observation of carbonate species in accordance with carbon (1*s*) signals (see [11]). The asymmetry in the carbon (1*s*) emission in the region 288.5–289.5 eV (Fig. 2a; peaks marked as 2 and 3) and the corresponding signals in the oxygen (1*s*) region (see [11]) could be attributed to anhydrous and basic carbonate species respectively.

In Fig. 3, we present the carbon (1*s*) spectra of FeTi samples under different experimental conditions, namely, the virgin and sputtered alloys exposed to air and oxygen respectively. Even after saturation coverage of oxygen on the sputtered alloy, the signals only due to adventitious carbon could be seen (see Fig. 3b). The high binding energy features that usually appear for the air exposed samples (see Fig. 3a; peaks marked as 2, 3 and 4) are completely absent. This observation clearly indicates that the carbonate species generated in air exposed samples could have arisen from the influence of atmospheric carbon dioxide. The result was corroborated by the oxygen (1*s*) signals (see [11]). For example, the air exposed sample gives a high binding energy feature at about 532.5–534.1 eV, whereas the oxygen exposed sample does not show any signal in this range. Figure 3a also suggests that the formation of anhydrous and basic carbonates of titanium (peaks 2 and 3; 288.0–289.0 eV) as well as of carbonate type species of iron (peak 4; 292.5 eV), in a similar way to that of the other systems discussed earlier.

It is to be noted that the concentrations of these carbonates are quite different for the various samples studied (see Figs 1–3) and depend on the nature of the alloy. This could be due to a number of factors, such as reactivity, defect structure, surface segregation, morphology, etc. The differences in the binding energy values of the anhydrous and basic carbonates could be explained on the basis of the electronegativity concept [15, 16]. Accordingly, the high binding energy peak in the doublet (Figs 1–3; peaks marked as 3) could be due to bicarbonates. The large amount of such species are indeed expected in the sense that the alloys' surface contains largely hydroxyl groups on the outer surface [2, 4, 10, 11]. The broad signals at 290.0–293.0 eV may also contain the basic carbonate as predominant species, for similar reasons, in accordance with the signals in the region 288.0–289.5 eV. However, it was not possible to differentiate clearly between these species, since the relative surface concentration of iron or nickel or copper is generally low compared to the other alloying element, namely, lanthanum or calcium or magnesium or titanium, in addition to their poor reaction with carbon dioxide.

Thus, the results unambiguously identify the presence of different carbonate species on various intermetallic compounds. They are produced by the interaction between the oxygen of the oxidized metal surface and the carbon atom of the carbon dioxide. That is, only after an initial reaction of the alloys with oxygen and/or moisture, the reaction of carbon dioxide would follow. Based on these results and the available information on the interaction of carbon dioxide on metal oxides from XPS [17–21] and IR [22–24] studies, we propose a model for the carbon dioxide adsorption and is presented in Fig. 4.

It is interesting to note that these systems behave differently when they are exposed to atmosphere. That is, the surface composition of the various species on the top few layers are quite different. For example, the $LaNi_5$ system shows large amounts of hydroxyl species; carbonate species predominate in the case of $CaNi_5$; whereas Mg_2Ni and Mg_2Cu indicate the distribution of both hydroxyl and carbonate species nearly equally; but an enhanced concentration of oxides are observed for FeTi [2, 10, 11]. This indicates that not only the competition between the different gas molecules, but also the reaction probability of the gas molecules with the surface plays an important role in producing the various surface species. The observed results are in qualitative agreement with the sorption studies of various gas molecules on different metal surfaces [25].

The present study also provides useful information on the concentration of various segregated elements at the alloy surface. In particular the transition metal content could be easily distinguished which, of course, are the key elements in the activation of hydrogen. For example, the enhancement of surface nickel concentration of $CaNi_5$ than that on $LaNi_5$ could be seen clearly from Fig. 1 (peaks marked as 4). That is, the increase in intensity of the signal (Fig. 1b; peak 4) reveals that more carbon dioxide molecules are adsorbed on the surface. In otherwords, nickel concentration is enriched on the $CaNi_5$ surface. This increase in nickel content explains the easier activation of $CaNi_5$ than of $LaNi_5$ as has been discussed elsewhere [10, 26]. Moreover, these results present direct evidence for the nickel rich surface than that from the nickel core levels, where the determination using nickel ($2p$) levels (especially for $LaNi_5$) is often difficult due to the overlap of nickel ($2p_{3/2}$) and lanthanum ($3d_{3/2}$) signals and the inadequate surface nickel content makes a poor resolution of the nickel ($2p_{1/2}$) signal.

Since carbon dioxide chemisorbs only to the submonolayer level, unlike oxygen and water vapour where the reactions upto a few hundred layers are known, it reflects directly the concentration of the surface species on the top few layers, which is important for the initial activation process. In addition, the multiplicity of the peaks in the spectra, analogous to the results for the simple and mixed oxides, indicates the heterogeneous character of the surface. As a result, it functions as a good probe in differentiating the various surface species.

Unfortunately, the concentration of surface carbonate species formed in well studied systems such as elemental metals and alloys (for example $LaNi_5$; see also Fig. 1a) is rather low [8, 9], which sometimes prevents their identification and the study of their reactivity of carbon dioxide, unlike the cases of $CaNi_5$, Mg_2Ni, Mg_2Cu and FeTi where large amounts of carbonates are seen (Figs 1b, 2 and 3a). Hence, in addition to the usual oxides and hydroxides on metal and alloy surfaces, which generally appear on the air exposed samples, the carbonates seem to be the additional contaminants on the surface. Therefore, importance has also to be given to the surface carbonates in devising methods for activation of the alloys. The carbon dioxide reaction on the surface can also play an important role in the segregation behaviour in alloys, like oxygen and moisture. However, quantitative measurements as well as detailed studies with oxygen, water vapour and carbon dioxide on the surface are needed to ascertain these findings.

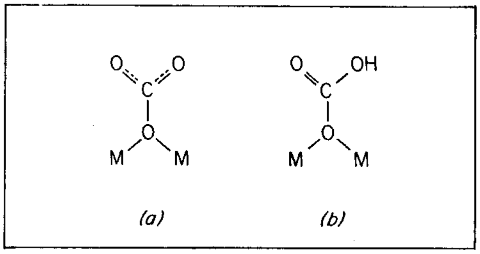

Fig. 4. Model of surface carbonate species: (a) anhydrous carbonate (CO_3^{2-}); (b) basic or bicarbonate (HCO_3^-).

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