

## Surface Studies of Some Hydrogen Storage Materials\*

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XPS, XAES and AES techniques have been applied to study the surface properties of certain hydrogen storage intermetallic compounds, namely,  $\text{LaNi}_5$ ,  $\text{CaNi}_5$ ,  $\text{Mg}_2\text{Ni}$ ,  $\text{Mg}_2\text{Cu}$  and  $\text{FeTi}$ . From these studies, it has been derived that the binary alloys undergo surface decomposition and subsequent oxidation upon exposure to air, resulting in a variety of oxygen containing species of the component elements. In addition, the surface compositions differ considerably for the various systems presented in this investigation, mainly because of their different segregation behaviours.

### Introduction

Among the intermetallic compounds available for hydrogen storage applications as 'rechargeable metal hydrides', the systems based on  $\text{AB}_5$ ,  $\text{AB}_2$ ,  $\text{A}_2\text{B}$  and  $\text{AB}$  have received

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considerable attention due to their ability to store large amounts of hydrogen /1,2/. Extensive studies have been reported on the bulk properties but not much information is available on the surface characteristics of these alloys. These materials have to be activated before they exhibit typical sorption processes, since, the alloy surfaces usually contaminated or passivated upon exposure to air. This deactivated surface in turn, retard the alloy-hydrogen reaction. Hence, the fundamental question that must be looked into, is, the phenomenon of surface poisoning.

The surface segregation of the constituent elements in binary alloy systems is well established. The segregated metal is prone to aerial oxidation. Thus, the oxidized metal surface hinders the interaction of the surface with hydrogen. On the basis of this, it may be probable that such intrinsic features are responsible for the regular activation procedures employed. The surface properties of the materials often play important role in determining sorption characteristics, such as, absorption and desorption processes. Therefore, the surface features of the intermetallic compounds are significant in regard to hydrogen uptake. We have reported several important aspects on the surface properties of these alloys elsewhere /2-10/. In this paper we present a comparative study on the surface properties of  $\text{LaNi}_5$ ,  $\text{CaNi}_5$ ,  $\text{Mg}_2\text{Ni}$ ,  $\text{Mg}_2\text{Cu}$  and  $\text{FeTi}$  alloys.

### Experimental

X-ray Photoelectron, X-ray induced Auger Electron and Auger Electron Spectroscopic (XPS, XAES & AES) data were obtained using an ESCALAB Mark II (UK) instrument. Commercial samples of the intermetallic compounds employed in this investigation were procured from Ergenics (USA). The experimental conditions and the procedures have been described elsewhere in detail /2,3,5,8/.

## Results and Discussion

XPS core level studies on  $\text{LaNi}_5$  and  $\text{CaNi}_5$  reveal that the surface of the air exposed samples are oxidized (Fig. 1).

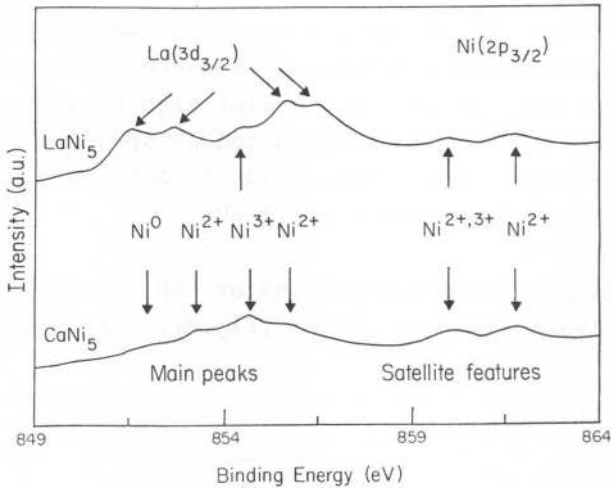


Fig.1. XPS lines of air exposed samples

As expected, the enrichment of La and Ca respectively on  $\text{LaNi}_5$  and  $\text{CaNi}_5$  were noticed.  $\text{La}(3d)$  and  $\text{O}(1s)$  spectra show that most of the La is present as  $\text{La}(\text{OH})_3$  ( $\sim 836.0$  eV) on the outer surface. However, upon sputtering for short periods,  $\text{La}_2\text{O}_3$  ( $\sim 834.8$  eV) predominates /2,10/. The shift in the binding energy values for the hydroxide and oxide species were clearly observed. Inspection of  $\text{C}(1s)$  region of  $\text{LaNi}_5$  suggests that additional oxygen is present on the sample as carbonate, though to a lesser extent /2,9,10/. Since  $\text{La}(3d_{5/2})$  region overlaps with  $\text{Ni}(2p_{3/2})$  region (see Fig.1), it complicates the analysis of the nature of the Ni species. However, the oxidized nature of the Ni species is deduced from the  $2p_{3/2}$ -satellite structures ( $\sim 861.5$ - $862.5$  eV), as can be seen from Fig. 1 and from the  $2p_{1/2}$ -emission line /2,8-10/.

In the case of  $\text{CaNi}_5$ , the  $\text{Ca}(2p)$  region indicates the presence of Ca in the oxidized form, as  $\text{Ca}(\text{OH})_2$  ( $\sim 347.6$  eV) and  $\text{CaO}$  ( $\sim 347.0$  eV) /2,8,9/. In addition, evidences have been shown for the existence of large amounts of carbonate species on the top few layers, as deduced from the  $\text{C}(1s)$  and  $\text{O}(1s)$  peak positions /2,9,10/. The  $\text{Ni}(2p_{3/2})$  spectra (Fig. 1) of  $\text{CaNi}_5$  clearly indicates that the surface Ni is completely oxidized. The spectra (both the core level and the satellite signals) also present distinctly the existence of various oxygenated Ni species, namely,  $\text{NiO}$  ( $\sim 854.3$  and  $\sim 861.5$  eV),  $\text{Ni}_2\text{O}_3$  ( $\sim 855.5$  and  $\sim 861.5$  eV) and  $\text{Ni}(\text{OH})_2$  ( $\sim 856.5$  and  $\sim 862.7$  eV).

The  $\text{Ni}(\text{LMM})$  Auger transitions of  $\text{LaNi}_5$  and  $\text{CaNi}_5$  reveal the passivated nature of Ni (Fig.2). The broad spectrum

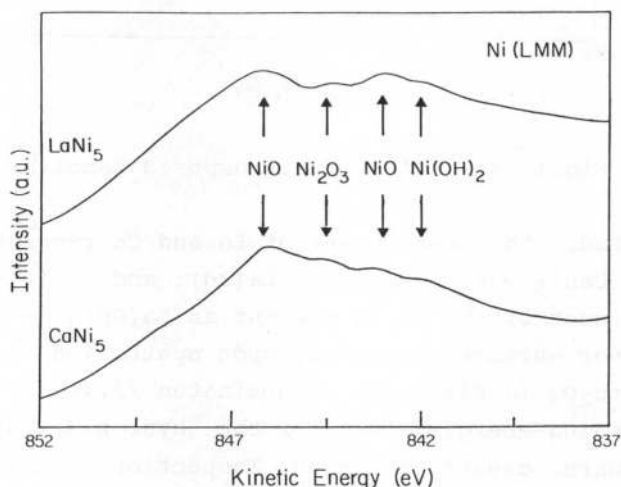


Fig.2. XAES lines of air exposed samples

itself is characteristic of the oxidized state of Ni. The presence of different types of Ni species, such as,  $\text{NiO}$  ( $\sim 843.3$  and  $\sim 846.0$  eV),  $\text{Ni}_2\text{O}_3$  ( $\sim 844.4$  eV) and  $\text{Ni}(\text{OH})_2$  ( $\sim 842.0$  eV) have also been deduced from the Auger lines and are indicated in the figure. It is interesting to note

from the results of both XPS and XAES that the surface Ni content on  $\text{CaNi}_5$  is higher than that observed on  $\text{LaNi}_5$  /8,10/. This surface enrichment was substantiated by the pronounced increase of adsorption of atmospheric  $\text{CO}_2$  on the oxidized surface /9/.

In a similar way, we have reported /2,6,7/ that the Mg-based alloys, such as,  $\text{Mg}_2\text{Ni}$  and  $\text{Mg}_2\text{Cu}$  undergo decomposition leading to pronounced enrichment of Mg on the surface resulting in the formation of a mixture of  $\text{MgO}$  (~ 50.4 eV) and  $\text{Mg(OH)}_2$  (~ 51.2 eV). Unlike the  $\text{LaNi}_5$  system, the hydroxide species are found to be smaller in amounts for the air exposed samples of the Mg-based alloys /10/. In the case of  $\text{Mg}_2\text{Ni}$ , the Ni is also oxidized in an identical fashion to that of  $\text{LaNi}_5$  and  $\text{CaNi}_5$ , producing various oxygenated species. However, the relative surface Ni concentration is little owing to its composition. On the otherhand, the  $\text{Mg}_2\text{Cu}$  system also shows a similar behaviour, namely, the oxidized nature of the surface copper species. Even though the  $\text{Cu}(2p_{3/2})$  region gives such information /10/, the  $\text{Cu(LMM)}$  Auger transition (Fig. 3) provides evi-

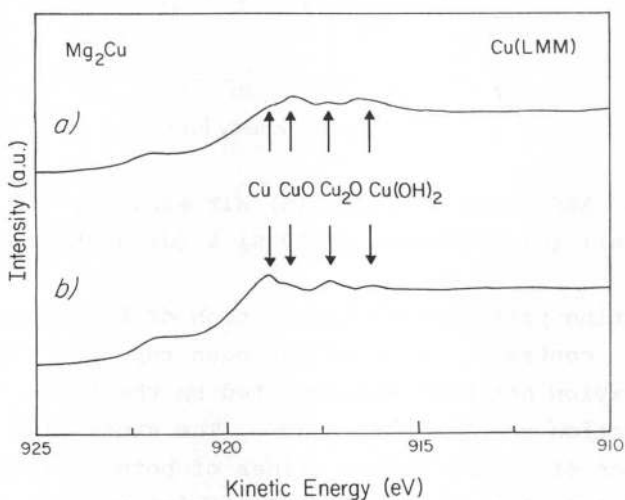


Fig.3. XAES line of  $\text{Mg}_2\text{Cu}$ : (a) air exposed & (b) sputtered

dence for the different species, namely,  $\text{Cu}_2\text{O}$  (917.0 eV),  $\text{CuO}$  (918.3 eV) and  $\text{Cu}(\text{OH})_2$  (916.3 eV). The carbonate species are also observed on the outer surface on both these alloys in a similar way to that of  $\text{AB}_5$  systems discussed earlier /9,10/.

AES studies on the air exposed FeTi alloy (Fig. 4) show the existence of Fe overlayers embedded on the Ti matrix

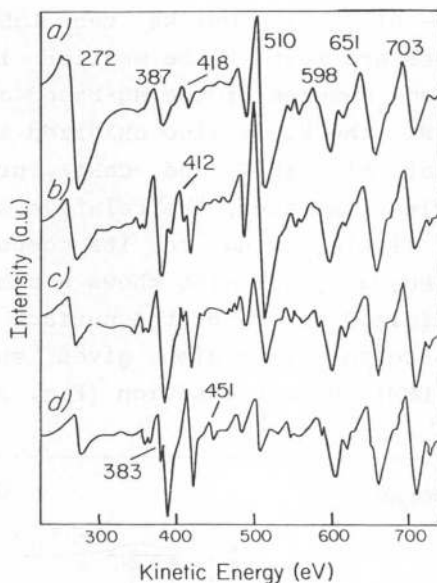


Fig.4. AES lines of FeTi: (a) air exposed; (b) sputtered (30 s); (c) sputtered (1800 s) & (d) sputtered (3600 s)

suggesting preferential segregation of Fe rather than Ti /2-5/, contrary to what has been reported /11,12/. This observation has been demonstrated on the basis of surface segregation phenomena /2,3,10/. The study also reveals the presence of higher valent oxides of both Fe ( $\text{Fe}_2\text{O}_3$ ) and Ti ( $\text{TiO}_2$ ) on the surface. Sputtering studies indicate the presence of various suboxides of the component elements of

the material. The results are supported by the XPS measurements reported earlier /2-5/. This system also shows the presence of carbonate type species, like many other alloys, upon exposure to air /9,10/.

### Conclusion

In summary, it is pointed out that all the alloys under investigation, namely,  $\text{LaNi}_5$ ,  $\text{CaNi}_5$ ,  $\text{Mg}_2\text{Ni}$ ,  $\text{Mg}_2\text{Cu}$  and  $\text{FeTi}$  undergo surface decomposition and oxidation, producing a variety of oxygen containing species of the constituent elements upon exposure to air. However, the concentrations of the products differ considerably based on their reactivity towards various gas molecules. Moreover, among the oxygenated species themselves, for example, oxides, hydroxides and carbonates, the concentrations vary markedly, especially for the non-transition metals. In addition, the surface compositions differ considerably from system to system mainly because of their very different surface segregation behaviours.

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