Hydrides of TbM₂ (M = Fe and Mn)

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Intermetallics TbFe₂, TbFeMn and TbMn₂ having C-15 cubic Laves phase structure, have been prepared and hydrided to varying values of H/M using gas phase method up to a saturation composition of H/M = 1.6. TbFe₂Hₓ samples show the formation of a metastable rhombohedral phase for higher values of x, which on equilibration with hydrogen transforms to cubic form. Unlike this, TbFeMn shows the existence of both hydrided and unhydrided phases for x ≤ 3.0 and for higher values of x, uniform hydriding takes place and a saturation composition of TbFeMnH₄.₈ which is characterized by cubic structure with 'a' = 8.137 Å, is obtained. For TbMn₂Hₓ, for x ≥ 1.2, the formation of a tetragonal phase is observed. Mössbauer study of TbFe₂Hₓ samples reveals that for TbFe₂, the Fe spins are aligned along (111) direction, which on hydriding become non-collinear and shift towards (100) direction for TbFe₂H₋₃.₁₅ composition. Mössbauer spectra of TbFeMn are complex and suggest a non-collinear spin alignment due to the existence of both ferromagnetic and antiferromagnetic interactions between transition metal elements and show a systematic decrease in magnetic field and magnetic transition temperature due to hydrogen incorporation in the matrix. Temperature programmed hydrogen desorption studies of TbFe₂Hₓ and TbFeMnHₓ samples exhibit broad peaks in the region 225-350 °C, due to overlap effects and peak maxima shift slightly towards higher temperature side with Mn substitution. Unlike this, TbMn₂Hₓ samples exhibit much better resolved TPR curves consisting of mainly three peaks placed over the region 275-400 °C, possibly because of the tetragonal structure of these samples.

Many intermetallics of rare earth and transition metals are known to absorb large quantities of hydrogen under moderate conditions of temperature and pressure. In the past few years a number of investigations¹⁻⁵ have been carried out to understand the hydriding characteristics of Laves phase cubic compounds because of the simplicity of their crystallographic and magnetic structures. The aim of these studies has been to establish the conditions and mechanism of hydride formation, changes in crystallographic and magnetic characteristics due to hydrogen incorporation and the degradation of AB₂ intermetallics during hydriding and dehydriding cycles. In this structure there are eight AB₂ formula units that constitute the unit cell and hydrogen atoms occupy the tetrahedral voids formed in this structure. There are 12 equivalent A₂B₂, γ-sites (96 g), 4 equivalent AB₃, β-sites (32e) and one B₄, α-site (8b) per formula unit available for hydrogen occupation. (The numbers in the brackets represent the Wyckoff notations of these sites.) However the relative occupancy of these sites and the sequence of filling of these sites are controlled by the relative size of different types of voids, minimum hydrogen-hydrogen separation and the electronic structure of rare earth and transition metal atoms. The occupancy of α-sites has not been well-established⁶⁻⁷ as for most of the systems the observed value of hydrogen content can be accounted by complete filling of only γ and β sites. A number of neutron diffraction studies⁸⁻¹⁰, carried out for different systems suggest that predominantly the γ sites, are occupied with some amount of hydrogen in β sites. This happens because of the higher affinity of hydrogen towards rare earth atoms as compared to the transition metal atoms, which is also reflected in the formation of their bulk hydrides. Temperature programmed hydrogen desorption studies can be used to get information about the occupation of hydrogen in different tetrahedral sites and their stability during desorption process as has been demonstrated by Park and Lee¹¹ and Kim et al.¹² for ErFe₂ and CeNi₂ systems, respectively. Based on the observance of three peaks in the TPR curves, Park and Lee¹¹ reported that there are two types of A₂B₂ sites and one type of AB₃ sites for hydrogen occupation in ErFe₂Hₓ system.

Another important aspect of the study of such hydrides, is to see the effect of hydrogen incorporation in the tetrahedral interstitial sites on the magnetic characteristics of these intermetallics, which have been extensively investigated by Mössbauer spectroscopy¹³⁻¹⁶. In general it has been observed that on hydriding, the isomeric shift increases and both internal hyperfine field and magnetic transition
temperature decrease due to the de-localization of charges and increased volume effects. It has also been reported that irrespective of the direction of spin orientation in RFe$_2$ compounds, Mössbauer spectra of ternary hydrides are a broad single sextet. The possible reasons for observing such a broad pattern are (a) the random occupation of interstitial sites by hydrogen atoms thereby locally affecting the direction of spin alignment which leads to a distribution of hyperfine interaction parameters, (b) the existence of more than one type of hydride phases of slightly different hydrogen stoichiometry and (c) the existence of very fine magnetic particles produced by the violent reaction of hydrogen with intermetallics, leading to the amorphisation of such material.

In the present communication we report the results of hydriding characteristics of isostructural TbM$_2$ intermetallics with M = Fe and Mn to see the effect of replacement of Fe by Mn on the crystallographic and magnetic characteristics of these hydrided samples using Mössbauer effect and powder X-ray diffraction techniques. Temperature programmed hydrogen desorption studies of TbM$_2$H$_x$ samples have been carried out to understand the filling of tetrahedral voids by hydrogen atoms.

**Materials and Methods**

Intermetallics were prepared by repeated arc melting of the constituent metals in ultra pure argon flow. The ingots so prepared were annealed at $\approx 1125$K in evacuated and sealed quartz tubes for 200 h. The formation of single phase intermetallics, with cubic C-15 structure, was confirmed by powder X-ray diffraction technique. The hydrides of the intermetallics with varying values of $x$ were prepared by standard gas phase method using Sievert type instrument made of stainless steel. Freshly crushed samples weighing approximately 0.5 to 1.0 gm were placed in the hydriding reactor evacuated to a pressure of $\approx 10^5$ torr at room temperature and exposed to varying pressures of hydrogen to get the desired composition of hydrides. For TbMn$_2$, one cycle of activation treatment is required before it starts absorbing hydrogen. For X-ray diffraction studies of these samples, monochromatic CuK$_\alpha$ radiation was used. $^{57}$Fe Mössbauer spectra were recorded at room temperature and 78K using a constant acceleration electromechanical drive coupled with a 1024 channel analyzer. The source used was $^{57}$Co in Rh matrix and absorbers contained approximately 0.25 to 0.30 mg $^{57}$Fe/cm$^2$. All isomeric shift values are reported with respect to iron metal at room temperature.

Temperature programmed hydrogen desorption spectra were recorded with a heating rate of 10 K/min. Samples weighing approximately 50 mg, were used for these experiments. The instrument consists of a tubular stainless steel reactor surrounded by a furnace. The evolved hydrogen gas was detected by gas chromatographic method using a molecular sieve column and helium as carrier gas. A thermal conductivity detector was used for the analysis of evolved hydrogen.

**Results and Discussion**

The intermetallics TbFe$_2$ and TbFeMn start absorbing hydrogen without any activation process. Unlike this, TbMn$_2$ needs one activation cycle before it can absorb significant amount of hydrogen. This activation process comprises of heating the sample in vacuum at 575K for about two hours followed by heating at the same temperature for about half an hour under hydrogen pressure of about five atmospheres. The sample when cooled to room temperature under hydrogen atmosphere exhibited hydrogen absorption. Before starting the actual measurements for hydrogen absorption for this sample, the hydrogen absorbed during activation process was completely desorbed by heating it at about 725K for two hours under vacuum.

The pressure composition isotherms, recorded at room temperature for these three intermetallics, are shown...
in Fig.1. From this figure it is clear that these intermetallics absorb hydrogen quantitatively on exposure to hydrogen and the saturation composition could be achieved at few atmospheres of hydrogen pressure. The observed saturation composition for these intermetallics are TbFe$_2$H$_{1.8}$, TbFeMnH$_{4.8}$ and TbMn$_{2}$H$_{4.5}$ with saturation value of H/M $\leq$ 1.6 and by adjusting the hydrogen pressure in the manifold, it was possible to prepare the hydrides with varying value of H/M.

An unusual metastable behaviour has been observed for the hydrides of TbFe$_2$. The hydride samples with $x \leq 3.15$, are found to be cubic in nature. But the samples with higher concentration of hydrogen show a rhombohedral distortion on initial exposure to hydrogen, as can be seen from Fig.2(c) where representative region of the X-ray diffraction pattern is shown for TbFe$_2$H$_{4.8}$. However when these samples were equilibrated under hydrogen pressure for extended time, the hydrided samples showed a cubic structure with systematic increase in unit cell volume with increase in hydrogen absorption as can be seen from Fig. 2(d). The observance of a metastable rhombohedral phase for TbFe$_2$H$_x$ is in conformity with the results reported by Berthier et al.\textsuperscript{17} Based on the volume analysis of the saturated hydrogen composition, the average increase in the unit cell volume corresponds to $\approx 3 \, \text{Å}^3$ per hydrogen atom.

The intermetallic TbFeMn, which has a cubic structure with a = 7.440 Å, when hydrided to different values of bulk H/M, shows the existence of both hydrided and unhydrided phases up to a bulk composition of H/M $\leq$ 1.0 and for higher values of H/M, the observed structure was cubic, with a saturation composition of TbFeMnH$_{4.8}$. The relative fraction of unhydrided phase decreased systematically with the increasing values of H/M and the unit cell volume of hydrided phase show a continuous increase. Essentially similar behaviour has been observed for ErFe$_2$H$_x$ and Zr$_{1-x}$Ho$_x$Co$_2$H$_x$ systems by Park and Lee\textsuperscript{11} and Ramesh et al.\textsuperscript{18} respectively. The saturation composition TbFeMnH$_{4.8}$ showed a volume increase of approximately 31% which is comparable to the value of 29% observed for TbFe$_2$H$_{4.8}$ and the average volume occupied by each hydrogen atom works out to be $\approx 3.4 \, \text{Å}^3$.

The X-ray diffraction pattern of TbMn$_2$ shows the formation of cubic Laves phase structure with a = 7.633Å. On hydriding, this sample retained its cubic structure for smaller values of ‘$x$’, however, the
samples with \( x \geq 1.2 \) show a tetragonal distortion as most of the peaks are found to be split into two peaks (viz. Fig. 3) where a representative region of the X-ray diffraction patterns is shown for some of these samples. It may be mentioned that similar splitting of different Bragg reflections has been reported for the hydrides of \( YFe_2 \), \( YMn_2 \) and some other systems\(^7\). These authors assigned it to the simultaneous formation of two metastable cubic hydrided phases with varying hydrogen composition. However in the present study, the relative intensity ratio of the splitted peaks corresponding to the different Bragg reflections of \( TbMn_2H_x \) is found to be significantly different as can be seen from Fig. 3, thereby ruling out the possibility of two different phases with varying values of hydrogen composition. All the Bragg reflections for different hydrogen compositions could be indexed in terms of tetragonal unit cell with \( c/a \) ratio \( = 0.512 \). For example for \( TbMn_2H_{1.5} \) the values ‘\( a \)’ and ‘\( c \)’ parameters are 10.435 and 5.339Å, respectively. This gives rise to a volume change of about 35\% due to hydrogen incorporation and the average volume occupied by each hydrogen atom works out to be 3.8Å\(^3\). The variation of unit cell parameters and unit cell volume as a function of hydrogen contents, is shown in Fig. 4. For \( TbMn_2H_x \) samples, relatively larger increase in unit cell volume was observed when the system changed from cubic to tetragonal form. Further increase in hydrogen concentration did not give rise to any significant volume change.

All these intermetallic hydrides were found to be stable at room temperature and retained their hydrogen concentration on exposure to atmosphere over a period of almost two years. These hydrides are not expected to loose hydrogen as their desorption plateau pressure lies below atmospheric pressure. Further it was possible to get back the cubic crystalline form for \( TbFe_2 \) and \( TbFeMn \) hydrides with decreasing values of \( x \) by slowly heating these samples to different temperatures. However, sudden heating of \( TbFe_2H_x \) samples at 775K lead to the formation of amorphous Fe and terbium hydride. \( TbMn_2H_x \) samples when heated up to different temperatures for the partial removal of hydrogen, transformed to cubic form on heating them up to different temperatures. On heating at 775K the hydrogen is completely lost and cubic crystalline \( TbMn_2 \) could be recovered.

\(^{57}\)Fe Mössbauer spectra of \( TbFe_2H_x \) samples, recorded at room temperature and 78K, are shown in Fig. 5. The observed spectra for \( TbFe_2 \) are complex and consist of two overlapping magnetic sextets of unequal intensity and characterized by different values of internal hyperfine field. For C-15 cubic Laves phase structure, the Fe atoms in a unit cell are placed at the corner sharing network of regular tetrahedrons with trigonal symmetry. Thus there are four sets of local principal e.f.g. axes with \( V_{zz} \) lying along the equivalent \( <111> \) directions for the four crystallographically equivalent Fe sites. These Fe sites are characterized by single values of isomeric shift and quadrupole splitting. However, depending on the spin alignment, the angle (\( \theta \)), between the directions of the principal electric field gradient and spin orientation, varies and the observed values of internal hyperfine field for these crystallographically equivalent Fe sites are found to be different because of the existence of anisotropic hyperfine fields. Thus for
Room temperature spectrum of TbFe$_2$H$_{1.15}$ shown in Fig. 5(g) is more like a single symmetric sextet which is characteristic of spin orientation along (100) direction as has been reported for a number of RF$_2$ intermetallics$^{22}$. Slight excess line width observed for this spectrum is arising due to the random occupation of hydrogen atoms in the tetrahedral sites thereby locally affecting the collinearity of spin alignment. The analysis of this room temperature spectrum gave $\delta = +0.25$ mm s$^{-1}$ and an internal hyperfine field $\sim 176$ KOe. This change in $\delta$ values is arising both due to the increase in unit cell volume and changed electron density in the 3d band of the Fe atoms. The observed value of internal hyperfine field at room temperature for TbFe$_2$H$_{3.15}$ is much less than the average value of the internal hyperfine field observed for TbFe$_2$ at room temperature. The 78K spectrum of this composition is again complex. This suggests a composition and temperature dependent spin orientation for TbFe$_2$H$_x$ system. The room temperature Mössbauer spectrum of TbFe$_2$H$_{4.8}$ is a paramagnetic doublet characterized by $\delta = 0.57$ mm s$^{-1}$ and $\Delta E_q = 0.45$ mm s$^{-1}$. These observations suggest that the magnetic transition temperature for TbFe$_2$H$_x$ decreases with increase in hydrogen contents as has been reported for a number of RF$_2$H$_x$ systems$^{25-27}$.

The room temperature and 78K Mössbauer spectra of TbFeMnH$_x$ samples which exhibited uniform hydriding, are found to be complex and do not show any specific spin orientation down to 78K. This is arising due to the magnetic frustration created in the lattice due to antiferromagnetic ordering between the Mn atoms$^{28}$ and ferromagnetic ordering between Fe atoms$^{29}$ as the magnetic ordering in these AB$_2$ type compounds is mainly decided by the most prominent B-B interaction. The presence of varying number of hydrogen atoms in the vicinity of Fe atoms, further affects the nature of magnetic interactions and the direction of spin alignment. The hydrogen incorporation leads to a qualitative decrease in the values of internal hyperfine field and magnetic transition temperature and an increase in isomeric shift values. These features are consistent with the behaviour observed for TbFe$_2$H$_x$ systems.

Temperature programmed hydrogen desorption measurements, carried out for varying values of $x$ for TbFe$_2$H$_x$, TbFeMnH$_x$ and TbMn$_2$H$_{1.15}$, are shown in Fig. 6. From this figure it is clear that for a given intermetallic the overall line shape of the TPD curve is not affected by the extent of hydrogen loading and in general same number of closely overlapping peaks
Fig. 6—Temperature programmed hydrogen desorption curves for (a) TbFe$_2$H$_{1.87}$, (b) TbFe$_2$H$_{2.97}$, (c) TbFe$_2$H$_{1.15}$, (d) TbFeMnH$_{2.2}$, (e) TbMn$_2$H$_{1.47}$, (f) TbFeMnH$_{1.8}$, (g) TbMn$_2$H$_{1.2}$, (h) TbMn$_2$H$_{2.6}$ and (i) TbMn$_2$H$_{4.5}$.

have been observed. For all the three intermetallics although some difference in the relative intensity of these peaks has been observed depending on the value of ‘x’. However for TbMn$_2$H$_x$, the temperature region over which hydrogen desorption occurs is much broader than that observed for TbFe$_2$ and TbFeMn. This may be because of the better stability of TbMn$_2$ hydrides and also to some extent due to the change in environment of hydrogen site brought about by the structural transformation of TbMn$_2$ on hydrogen incorporation. Further, the temperature at which hydrogen desorption initiates is systematically increased with Mn substitution. The temperature region, over which hydrogen desorption occurs for these intermetallics, is much smaller than that observed for the hydrides of isostructural TbCo$_2$ and TbNi$_2$, both of which form amorphous hydrides$^{36}$, and ErFe$_2$H$_3$, reported by Park and Lee$^{37}$. Based on the shape of these TPR curves, which is not appreciably affected for different hydride compositions, it is inferred that for these compositions, most of the hydrogen atoms are mainly occupying the γ-sites. If hydrogen atoms had also been placed at the other two α and β sites, there should have been significant difference in their hydrogen desorption temperatures because of the difference in the constitution of these sites.

The two factors, which mainly decide the stability of hydride phases of these terbium intermetallics, are the electron exchange between hydrogen and transition metal atoms and the relative volume of the tetrahedral voids, which are to be occupied by hydrogen. For TbMn$_2$ the volume of the tetrahedral voids is slightly larger than that of TbFe$_2$ as the ‘a’ values, for these two intermetallics, are 7.633 and 7.355Å respectively. Further the large positive shift of $\approx 0.64$ mms$^{-1}$ observed in the room temperature values of the chemical shift of TbFe$_2$ and TbFe$_2$H$_{4.8}$ cannot be completely accounted in terms of the increased volume of the unit cell as suggested by Weisenger$^{31}$ who had invoked the transfer of 4s electrons of Fe to the hydrogen atoms as the Fe 3d states are not appreciably affected by hydrogen incorporation in the lattice. Similar suggestions regarding the 4s electron transfer from Fe to hydrogen site have been made by Gupta$^{32}$ as well as Switendick$^{33}$. This 4s electron transfer has also been substantiated from the XPS studies of Schlapbach$^{34}$ for ZrMn$_2$H$_3$ system. The 4s electron transfer is expected to be easier for Mn as compared to that of Fe because of the difference in their electronegativity values, which are 1.55 and 1.83, respectively. Both these factors suggest a better stability for TbMn$_2$H$_x$ samples as compared to TbFe$_2$H$_x$ samples, which is in agreement with the results reported here.

It can be concluded that in the present communication we have reported the formation of various hydride compositions for isostructural TbFe$_2$, TbFeMn and TbMn$_2$ with a saturation value of H/M equal to $\approx 1.6$ and their crystallographic characteristics have been reported. Based on Mössbauer effect studies, it is observed that the hydrogen incorporation in TbFe$_2$ leads to non-linear spin alignment and in general the strength of magnetic interactions is decreased due to increased unit cell volume and partial charge transfer. Based on temperature programmed hydrogen desorption studies it is inferred that primarily the γ-sites are being occupied by hydrogen atoms in these intermetallic hydrides.
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