Investigation of $Y_6Mn_{23}$ and $YMn_{12}$ intermetallic alloys under high hydrogen pressure

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Abstract. Among three intermetallic compounds existing in Y-Mn system the YMn$_2$ and $Y_6Mn_{23}$ can easily form interstitial hydrides while for YMn$_{12}$ existence of hydride has never been reported. At moderate hydrogen pressure YMn$_2$ and $Y_6Mn_{23}$ transform into YMn$_2H_{4.5}$ and $Y_6Mn_{23}H_{25}$ respectively. At high hydrogen pressure the YMn$_2$ (C15 or C14 parent structure) forms a unique YMn$_2H_6$ (s.g. $Fm\bar{3}m$) complex hydride of fluorite structure in which one Mn atom Mn(1) and Y randomly occupy the 8c sites while second manganese (Mn2) in position 4a forms complex anion with 6 hydrogen atoms located in positions 24e. Formation of YMn$_2H_6$ independently of the structure of parent phase (C14 or C15) as well as occupation of the same site (8c) by Y and Mn(1) atoms suggested that also $Y_6Mn_{23}$ and YMn$_{12}$ could transform into YMn$_2H_6$-type hydride in which suitable number of Y atoms will be substituted by Mn(1) in the 8c positions. This assumption was confirmed by exposing $R_6Mn_{23}$ and RMn$_{12}$ to 1 GPa of hydrogen pressure at 1000°C. Formation of $(R_xMn_{2-x})MnH_6$ (where $x = 18/29$ or 3/13 for $R_6Mn_{23}$ and RMn$_{12}$ hydrides respectively) was confirmed by XRD. Hydrogen concentration in both $R_6Mn_{23}$ and RMn$_{12}$ based hydrides reached $H/Me = 2$ thus value two times higher than in $R_6Mn_{23}H_{25}$.

1. Introduction

In a former research we demonstrated that treatment of intermetallic alloys under high hydrogen pressure can lead to formation of novel hydrides in materials considered as non-hydride forming or in those which at moderate hydrogen pressure can form hydrides but with relatively low hydrogen-to-metal ratios [1].

The Y-Mn intermetallic compounds attract particular interest due to their unusual structural and magnetic properties. These properties can be altered by hydrogenation (deuteration) and a number of papers were published on hydrogen influence on structural, magnetic and electronic properties of YMn$_2H_x$ ($x \leq 4.5$) [2,3] and $Y_6Mn_{23}H_y$ ($y \leq 25$) [4]. Let us remark that $H/(Y+Mn)$ ratio for YMn$_2H_{4.5}$ is more than 50 % higher than for $Y_6Mn_{23}H_{25}$ and hydride of RMn$_{12}$ has never been reported. This can be interpreted in terms of great difference in hydrogen pressures necessary to form hydride of yttrium and that of manganese. Yttrium forms hydrides (metallic YH$_2$ and insulating YH$_3$) at $H_2$-pressure smaller than 1 MPa [5] while for syntheses of $hcP$ MnH$_{0.8}$ [6] or $fcc$ MnH$_{0.6}$ [7] pressures higher than 0.5 GPa($H_2$) are needed. Therefore it can be expected that formation of hydrides in alloys with higher Mn concentration (like YMn$_{12}$) would be possible but at sufficiently high hydrogen pressure. On the
other hand exposure of Y₆Mn₂₃ at high hydrogen pressure can result in syntheses of novel hydride (hydrides) not available at low hydrogen chemical potential (i.e. low hydrogen pressure).

Recently we found new, intriguing hydrides RMn₂₃H₆ (R = Y, Er, Ho, Dy, Gd), by exposing RMn₂₃ Laves C14 or C15 alloys at 1 GPa(H₂) and 398 K [1,8-10]. These hydrides are formed through total reconstruction of the parent (C14 or C15) lattice. They have Fm3m crystalline symmetry in which one Mn atom, located in 4a sites is surrounded by 6 H (or D) atoms while the other one, together with Y atoms, occupy randomly the 8c sites. XRD patterns for YMn₂₃ and YMn₂₃D₆ are shown in figure 1. Positions of Mn, Y and D atoms in the Fm3m structure of YMn₂₃D₆ are represented in the figure 2.

![Figure 1](image1.png)  
**Figure 1.** XRD patterns for YMn₂₃D₆ (above) and C15 YMn₂₃ (below).

![Figure 2](image2.png)  
**Figure 2.** Fm3m structure of YMn₂₃D₆. The largest balls represent yttrium, medium – manganese and smallest - deuterium.

Having in mind that:
- manganese has tendency to form (MnH₆)ₓ anions network with R and another Mn atoms as their cation partners;
- the (MnH₆)ₓ anions are mainly responsible for properties of RMn₂₃H₆ hydrides [10];
- RMn₂₃H₆ hydrides of Fm3m symmetry can be formed from different parent structures (C14 or C15);
- the RMn₂₃H₆ formation is sensitive for substitution of manganese in 4a sites but insensitive for substitution of rare earth in the 8c sites [11];
- yttrium (or rare earth) coexists with manganese in 8c sites of complex RMn₂₃H₆ hydrides.
- Y₆Mn₂₃ can be found in products of YMn₂₃H₆ thermal decomposition,

we assumed that RMn₂₃H₆ - type hydrides can be formed also from other, manganese rich R-Mn especially from Y₆Mn₂₃ and YMn₁₂.

### 2. Experimental

Ingots of Y₆Mn₂₃ and YMn₁₂ were prepared by induction melting of 99.9 % pure elements in a water-cooled copper boat under argon atmosphere followed with 10 days long annealing at 800°C. Then ingots were crushed into powder and hydrided in high hydrogen pressure apparatus described elsewhere [12]. High pressure hydrogen treatment has been carried out at 1 GPa(H₂) and 100°C for 5 days. The XRD patterns were measured with a D8 Brucker diffractometer equipped with a rear graphite monochromator using Cu Kα radiation.
3. Results and discussion

The XRD patterns of parent and hydrogenated Y\textsubscript{6}Mn\textsubscript{23} alloy are shown in figure 3a. They are substantially different in spite that both belong to the same space group \textit{Fm\textsubscript{3}m}. The characteristic feature of the hydride pattern is that it corresponds to a single phase which is identical with pure YMn\textsubscript{2}H\textsubscript{6} hydride. This can be explained by hydrogen induced radical restructurization of the parent Y\textsubscript{6}Mn\textsubscript{23} lattice containing four formula units (116 atoms) in a unit cell. During hydrogenation process the complicated Y\textsubscript{6}Mn\textsubscript{23} lattice fully transforms into more simple \textit{Fm\textsubscript{3}m} structure in which metallic atoms can occupy (just as in YMn\textsubscript{2}H\textsubscript{6}) only two positions: 4a and 8c. In positions 4a only Mn atoms covalently bounded with six H atoms can be located. The 8c position is statistically occupied by yttrium and remaining manganese atoms. The structures of hydrides derived from Y\textsubscript{6}Mn\textsubscript{23}, YMn\textsubscript{12} and YMn\textsubscript{2} differ only by the manganese-to-yttrium atomic ratio in randomly occupied 8c positions. From simple calculation the Mn/Y = 1 for YMn\textsubscript{2}H\textsubscript{6} while for hydride formed from Y\textsubscript{6}Mn\textsubscript{23} the Mn/Y ratio in 8c positions should be 40/18.

For the first time we obtained YMn\textsubscript{12} based hydride with XRD pattern shown in figure 3b. In contrast to Y\textsubscript{6}Mn\textsubscript{23} we could not yet form a single phase hydride from YMn\textsubscript{12}. However, the amount of the YMn\textsubscript{2}H\textsubscript{6} – type hydride gradually increased when YMn\textsubscript{12} was repeatedly treated by high hydrogen pressure. Assuming complete transformation of YMn\textsubscript{12} into the YMn\textsubscript{2}H\textsubscript{6} – type hydride the Mn/Y atomic ratio in its 8c site should be as high as 23/3.

Finally, let us remark that amount of hydrogen absorption in novel hydrides derived from Y\textsubscript{6}Mn\textsubscript{23} and YMn\textsubscript{12} alloys corresponds to H/(Y+Mn) = 2 atomic ratio, thus it is two times higher than that in Y\textsubscript{6}Mn\textsubscript{23}H\textsubscript{25} reported by Pourarrian [4].

3. Conclusions

Under high hydrogen pressure we succeeded for the first time to synthesize hydride of YMn\textsubscript{12} and a novel hydride of Y\textsubscript{6}Mn\textsubscript{23} with hydrogen concentration two times higher than in Y\textsubscript{6}Mn\textsubscript{23}H\textsubscript{25} hydride known so far. It is especially interesting that hydrides received under high hydrogen pressure from

![Figure 3. XRD patterns of parent and hydrogenated Y\textsubscript{6}Mn\textsubscript{23} (a) and YMn\textsubscript{12} (b) alloys](image-url)
YMn$_2$, Y$_6$Mn$_{23}$ and YMn$_{12}$ in principle are isostructural and have cubic structure with $Fm\overline{3}m$ space group. All three hydrides have one Mn atom in 4a position which forms a complex anion with 6 H atoms. Remaining manganese and yttrium atoms occupy randomly the 8c site with different manganese-to-yttrium occupancy ratio.

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