Hydrogen Storage Properties of Oxygen modified AB_2 type Metal Hydride Alloy

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Introduction

A promising application for metal hydrides (MH) is hydrogen storage and its supply to Proton Exchange Membrane Fuel Cells (PEMFC's) in material handling units, underground mining vehicles and marine applications. Of the numerous MH materials, AB_2 type alloys (A=Ti+Zr; B=Mn+Cr+V+Fe+Ni+…) have shown to be very promising. Hydrogen sorption properties of these materials can be easily tuned by the variation of their composition.

The effects of stoichiometry and alloying elements on the hydrogen storage properties of Ti based AB_2 alloys have been extensively investigated, both in the past [1,2] and more recently [3,4]. The recent studies were mainly focused on the development of efficient MH materials for hydrogen storage and compression applications. It has been shown that small changes in the composition of the alloys significantly influence on the PCT properties of the MH and the usable hydrogen capacity at the operating pressure – temperature conditions.

A multi component AB_2 type hydrogen storage intermetallic alloy ($A=Ti_{0.85}Zr_{0.15}$, $B=Mn_{1.22}Ni_{0.22}Cr_{0.2}V_{0.3}Fe_{0.06}$; V and Fe were introduced as a commercial Ferrovanadium) was investigated in this work. The intermetallic specified above was also modified by oxygen to yield the composition $AB_2O_{0.05}$. The oxygen was introduced by adding TiO_2 to the charge, with corresponding decrease of the Ti amount, followed by arc melting and annealing at the same conditions as for the oxygen free AB_2-type alloy.

Experimental

- Elemental Ti, Zr, Cr, Mn, Ni, V and Fe introduced as commercial Ferrovanadium were used to prepare a multi component AB_2 alloy via arc-melting under an Ar atmosphere followed by annealing at 950 °C for 24 hrs.
- The alloy was modified by introduction of oxygen by adding TiO_2.
- Elemental analysis were carried out on crushed sections of the prepared alloys using SEM (Leo 1240) with EDS (INCA software).
- The alloys were characterised by room temperature XRD (Cu-K_α) both before and after hydrogen sorption measurements.
- Hydrogen absorption studies (sample weight ~1 g; T=20 °C, P_0~30 bar; no vacuum heating before first hydrogenation; further hydrogenations were preceded by heating the sample in dynamic vacuum to T=300 °C during 1 hour).
- PCT properties were measured at 20 °C, up to 100 bar H_2 using a volumetric Sieverts system (PCTPRO 2000). Prior to measurements an activation sequence was performed in situ at 300 °C for 3 hours under vacuum, followed by an absorption isotherm at room temperature.

Compositional and Morphological Properties

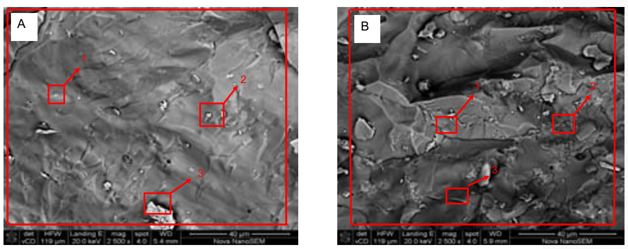

Figure 1: (A) SEM image of $Ti_{0,85}Zr_{0,15}Cr_{0,2}Mn_{1,22}Ni_{0,22}V_{0,3}Fe_{0,06}$, (B) $Ti_{0,85}Zr_{0,15}Cr_{0,2}Mn_{1,22}Ni_{0,22}V_{0,3}Fe_{0,06}O_{0,05}$

Table 1: Summary of compositional properties of the multi component AB2 type alloys prepared via arc-melting

Components	Content, wt. %									
	Nominal	Measured Fig. 1 (a) $Ti_{0.85}Zr_{0.15}Cr_{0.2}Mn_{1.22}Ni_{0.22}V_{0.3}Fe_{0.06}$				Nominal	Measured Fig. 1 (b) $Ti_{0.85}Zr_{0.15}Cr_{0.2}Mn_{1.22}Ni_{0.22}V_{0.3}Fe_{0.06}O_{0.05}$			
		Total area	Point 1	Point 2	Point 3		Total area	Point 1	Point 2	Point 3
A (Ti)	24.922	26.44	25.08	23.82	29.86	24.8	24.31	27.07	28.02	26.44
A (Zr)	8.375	8.72	9.86	9.27	8.39	8.335	9.45	9.53	8.63	12.3
B (Cr)	6.365	4.9	5.3	5.66	3.77	6.334	6.09	6.97	5.49	8.08
B (Mn)	41.026	39.19	39.8	39.89	35.42	40.826	39.43	32.3	31.34	28.9
B (Ni)	7.906	9.31	8.46	6.8	11.72	7.868	6.31	6.83	7.81	5.82
B (Fe)	2.051	1.99	2.07	2.15	1.78	2.041	2.4	2.25	2.34	2.7
B (V)	9.355	9.45	9.44	8.75	9.06	9.309	9.04	10.52	9.33	10.21
Impurity: (O)	-	-	-	3.66		0.487	2.98	4.52	7.04	5.56

- SEM / EDS results generally confirmed the XRD data, exhibiting the major phase (matrix) of the composition corresponding to A:B≈2, where the measured concentrations of the metals corresponds to the nominal content of the alloy.
- EDS results shows that the average oxygen impurity of 5.025 wt.% for the modified sample (B), while sample (A) only detected oxygen at point 3, this can be attributed mainly to the use of FeV as it contain small amounts of impurities.

Structural Properties

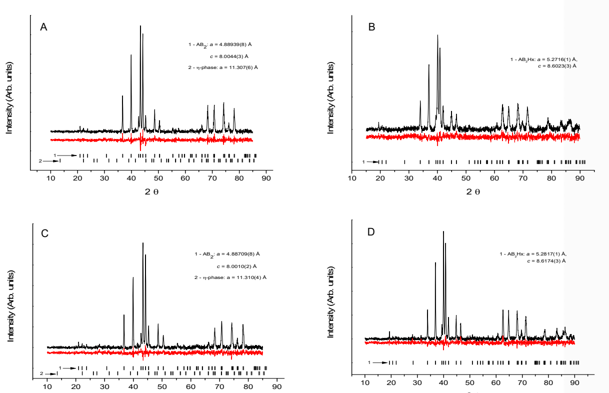

Figure 2: (A) XRD pattern of as prepared $Ti_{0,85}Zr_{0,15}Cr_{0,2}Mn_{1,22}Ni_{0,22}V_{0,3}Fe_{0,06}$, (B) hydrogenated $Ti_{0,85}Zr_{0,15}Cr_{0,2}Mn_{1,22}Ni_{0,22}V_{0,3}Fe_{0,06}$ (C) as prepared $Ti_{0,85}Zr_{0,15}Cr_{0,2}Mn_{1,22}Ni_{0,22}V_{0,3}Fe_{0,06}O_{0,05}$, (D) hydrogenated $Ti_{0,85}Zr_{0,15}Cr_{0,2}Mn_{1,22}Ni_{0,22}V_{0,3}Fe_{0,06}O_{0,05}$

- Major phase for as prepared alloys (A) and (C) is C14 Laves (AB_2)
- Both alloys (A) and (B) has impurity phase h-phase ($Ti_4Fe_2O_{0.4}$) corresponding to 1,7 and 2,3 wt.% respectively.
- The hydrogenated samples (B) and (C) showed one phase AB2Hx

Hydrogen Sorption Studies

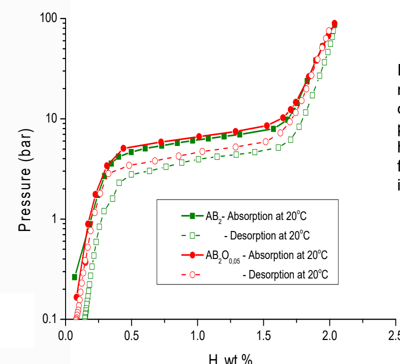

Figure 3: H_2 absorption and desorption isotherms for the studied AB_2 type alloys.

It can be seen that the oxygen modification did not significantly change the hydrogen sorption performance, except for slightly higher H_2 equilibrium pressures for the oxygen-modified intermetallic.

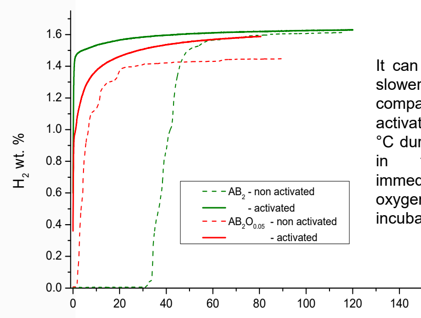

Figure 4: H_2 absorption kinetics (T=20 °C, P(H_2)= 20 bar) for the studied AB_2 type alloys.

It can be seen that despite slightly slower kinetics for $AB_2O_{0.05}$ as compared to oxygen-free AB_2 after activation by vacuum heating to 300 °C during 1 hour, it starts absorb H_2 in the non-activated state immediately while the non-activated oxygen-free sample has an incubation period about 30 minutes.

Conclusion

- Both alloys have shown to be promising hydrogen storage materials due to their relatively high H storage capacity (1.8 wt. %) and plateau pressures at room temperature below 5 bar.
- The addition of small amounts of oxygen does not change the hydrogen absorption performance, but improves the absorption kinetics of the alloy.

References

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