PREPARATION AND ANALYSIS OF Fe-Zr, Fe-Ti, AND Fe-V COMPOSITES FOR HYDROGEN STORAGE

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Abstract

Fe, Ti, V, and Zr composites were prepared by mixing and dry milling of ferrihydrite with V, TiH_2, and ZrH_2 powders. The samples were annealed in vacuum and hydrogen atmosphere during measurements of the temperature dependence of their magnetic moments in temperature range 20 – 800 °C. Pure metal -Fe, -Zr; Fe_2Zr, TiFe, and Ti_2Fe intermetallic phases and various Fe, Zr, V and Ti oxides were formed by these heat treatments.

Introduction

Transition metals based composites still belong to candidates for hydrogen batteries. Their practical application, however, are connected with some difficulties due to high temperature and relatively slow kinetics of hydrogen desorption of absorption. Their nanocrystalline states exhibit much faster kinetics and lower temperature of hydriding/dehydriding in comparison with coarse grained materials with the same composition [1-3].

It was shown that Zr-rich phases disproportionate and reproportionate by absorbing of hydrogen and $FeZr_2$ and $FeZr_3$ were observed. Zr_2FeH_5 was formed by hydride absorption at room temperature. The disproportionation of Zr_2Fe was unstable and it was very quickly followed by a reproportionation to Fe_2Zr [4-5]. Mechanical alloying of a $Ti_{45}Zr_{38}Ni_{17}$ powder mixture formed an amorphous phase, but subsequent annealing caused the formation of an icosahedral quasicrystalline phase with a small amount of the Ti_2Ni-type crystal phase [6]. After high-pressure hydrogenation at 573 K at a hydrogen pressure of 3.8 MPa, the amorphous phase transformed to a TiH_2-type hydride, while the icosahedral phase was structurally stable even after the hydrogenation.

Experimental details

TThe samples were prepared by from pure ferrihydrite (Sigma Aldrich) and V, TiH_2, and ZrH_2 (Alfa Aesar) powders by dry ball milling or mixing in an agate mortar. The original composition of the composites was 39 wt% of ferrihydrite and 61 wt% of the V, TiH_2, and ZrH_2. The as-mixed powders were compressed into pellets and annealed during the measurement of the temperature dependence of magnetic moment in temperature range 20°C - 800°C in vacuum (10^{-4} Pa) and in the hydrogen (5N). Magnetic measurements were carried out using vibrating sample magnetometer in 50 Oe external field.

The X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) were applied for structure and phase analysis. XRD was carried out using X'Pert diffractometer and CoK radiation with qualitative analysis by HighScore® software and the JCPDS PDF-4 database. For a quantitative analysis HighScore plus® with Rietveld structural models based on the ICSD database was applied. ^{57}Fe Mössbauer spectra were measured using ^{57}Co/Rh source in standard transmission geometry with detection of 14.4 keV -rays. The computer processing of the spectra for phase analysis was done using CONFIT package [7].

Results

The XRD phase analysis of the as-mixed samples exhibited mainly presence of the precursors. The composites prepared in an agate mortar contained 61 wt% V and 61 wt% TiH_2 which almost identical with the nominal composition. The dry milled V and TiH_2 based samples showed also the original precursor phases of nominal composition but in ZrH_2 based composite formation of magnetite (33 wt%) and ZrH_2 (68 wt%) was observed. The Mössbauer spectra correspond to the ferrihydrite in V and TiH_2 composites and ferrihydrite and magnetite, -Fe and $ZrFe_2$ in ZrH_2 composite. Changes in the phase compositions during the 20°C - 800°C annealing were detected by the measurement of the temperature dependence of the magnetic moments. The Curie temperatures of -Fe, magnetite, hematite and Fe_2Zr phases were observed there. The presence of these magnetic phases was confirmed by XRD and Mössbauer phase analysis. The phase compositions of the annealed samples are given in Tables 1 and 2. There are significant differences after annealing in vacuum and in hydrogen. The hydrogen atmosphere helped to reduce ferrihydrite to pure iron and to form of intermetallic phases. The powders contain small or negligible amount of oxides even after the handling in ambient atmosphere by preparation of the samples for XRD and Mössbauer measurements. The vacuum annealing caused formation of Zr, Ti, and V oxides but their formation after the annealing during the sample preparation for the phase analysis cannot be excluded. Iron ions embedded in the matrix of oxides stabilize of tetragonal (t-ZrO2) form, which is present in the sample together with the stable monoclinic (m-ZrO2) form. This is confirmed by the presence of 0.06 atom fraction of Fe(III) detected by means MS.

Table 1. Results of the phase analysis of the annealed composites prepared by mixing in an agate mortar.

XRD [wt. %]				
TiH_2 + ferrihydrite (vacuum)	2 $FeTiH_{0.06}$	10 Ti_2Fe	42 -Fe	46 Ti_xO
TiH_2 + ferrihydrite (hydrogen)	7 $FeTiH_{0.02}$	10 Ti_2Fe	11 FeTi	71 $TiO_{0.325}$
V + ferrihydrite (vacuum)	11 V_2H	25 $VO_{0.03}$	64 Fe_3O_4	
V + ferrihydrite (hydrogen)	21 V_2H	70 -Fe	9 Fe_3O_4	
Mössbauer spectroscopy [Fe atom fractions]				
TiH_2 + ferrihydrite (vacuum)	0.39 -Fe	0.32 Fe-Ti	0.29 Fe(III)	
V + ferrihydrite (vacuum)	0.93 Fe_3O_4	0.07 Fe(III)		
V + ferrihydrite (hydrogen)	0.97 -Fe	0.03 Fe(III)		

Table 2. Results of the phase analysis of the annealed composites prepared by dry ball milling.

XRD [wt. %]				
TiH_2 + ferrihydrite (vacuum)	34.5 TiH_2	32.4 Fe_3O_4	9 Fe	24.1 $TiO_{0.48}$
ZrH_2 + ferrihydrite (vacuum)	53.9 m-ZrO_2	14.7 t-ZrO_2	7.6 -Fe	23.9 -Zr
V + ferrihydrite (vacuum)	10.7 V_2H	24.6 $VO_{0.03}$	64.7 Fe_3O_4	
V + ferrihydrite (hydrogen)	20.8 V_2H	69.9 -Fe	9.3 Fe_3O_4	
Mössbauer spectroscopy [Fe atom fractions]				
TiH_2 + ferrihydrite (vacuum)	0.35 -Fe	0.6 Fe_3O_4	0.05 Fe(III)	
ZrH_2 + ferrihydrite (vacuum)	0.06 Fe(III)	0.14 -Fe	0.8 Fe_2Zr	
ZrH_2 + ferrihydrite (hydrogen)	0.07 Fe(III)	0.59 -Fe	0.34 Fe-Zr-H	

Conclusions

From the above results we can conclude that formation of intermetallic phases which can be interesting for hydrogen absorption can be yielded by annealing in hydrogen atmosphere. The presence of FeTi, Ti_2Fe and Fe_2Zr intermetallic was confirmed but Zr_2Fe and Zr_3Fe phases well known for their ability to store hydrogen were not detected in the Zr based samples.

References

1. W. Liu, H. Wu, Y. Lei at all. *J. Alloys Comp*, **261** (1997) 289.
2. T. Spassov, U. Köster, *J. Alloys Comp*, **287** (1999) 243.
3. L.E.A. Berlouis, E. Cambera, E. Hall-Barientoss at all., *J. Mater. Res*, **16** (2001) 45.
4. A. Zaluska, L. Zaluski, J. O. Strom-Olsen, *Appl. Phys. A*. **72** (2001) 157-165.
5. T. Klassen, R. Bohn, G. Fanta, at all., *Z. Metallkde* **94** (2003) 610-614.
6. A. Takasaki, V.T.Huett, K.F. Kelton, *J non-cryst solids*, **334-335** (2004) 457-460.
7. T. Žák, *Mössbauer Spectroscopy in Materials Science*, edited by M. Miglierini and D. Petridis, (Dordrecht: Kluwer Academic Publishers), 1999, pp. 385-389.

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