



koncentrací pyritu a markazitu. Další výsledky jako uspořádanost-neuspořádanost struktura a poměr zastoupení Fe a S ve struktuře pyritu a markazitu, které ovlivňují především kinetiku chemických reakcí při zvětrávání sulfidů a jejich termodynamickou stabilitu, nebyly dostatečně přesné a věrohodné, a tudíž pro geochemické modelování nebyly použitelné.

Literatura

Dollase W. A. (1986): Correction of intensities for preferred orientation in powder diffractometry: Application of the March model., *J. Appl. Cryst.*, **19**, 267-272.

Hastings J. B., Thomlinson W., Cox D. E. (1984): Synchrotron X-ray powder diffraction., *J. Appl. Cryst.*, **17**, 85-89.

Johnson N. E., Pollack S. S., Frommell E. W., Eldredge P. A. (1995): Powder diffraction analysis of an interstratified marcasite/pyrite structure., *Powder Diffraction*, **10**(3), 198-203.

March A. (1932): Mathematische Theorie der Regelung nach Korngestalt bei affiner Deformation., *Z. Kristallogr.*, **81**, 285-297.

Rietveld H. M. (1969): A profile-refinement method for nuclear and magnetic structures., *J. Appl. Cryst.*, **2**, 65-71.

Sasaki K., Kono H., Inagaki M. (1994): Structure strain in pyrite evaluated by X-ray powder diffraction., *J. Mater. Sci.*, **29**, 1666-1669.

Will G., Bellotto M., Parrish W., Hart M. (1988): Crystal structures of quartz and magnesium germanate by profile analysis of synchrotron-radiation high-resolution powder data., *J. Appl. Cryst.*, **21**, 182-1991.

Young R. A., Sakthivel A., Moss T. S., Paiva-Santos C. O. (1995): DBWS-9411, an Upgrade of the DBWS*. * Programms for Rietveld Refinement with PC and Mainframe Computers., *J. Appl. Cryst.*, **28**, 366-367.

Young R. A., Sakthivel A., Moss T. S., Paiva-Santos C. O. (1995): DBWS-9411, an Upgrade of the DBWS*. * Programms for Rietveld Refinement with PC and Mainframe Computers., *J. Appl. Cryst.*, **28**, 366-367.

SL2

CHANGES IN PHASE COMPOSITION OF $\text{NaAlH}_4 + \text{FeCl}_2$ COMPLEX HYDRIDE EXPOSED TO AIR

P. Roupcová^{1,2}, O. Schneeweiss¹

¹Institute of Physics of Materials, Academy of Sciences of Czech Republic v.v.i., Žitkova 22, 616 62 Brno, Czech Republic

²Institute of Material Science and Engineering, Faculty of Mechanical Engineering, Brno University of Technology, Technická 2, 616 69 Brno, Czech Republic, roupcova@ipm.cz

Keywords: Mössbauer spectroscopy, X-ray diffraction, hydrogen absorbing materials

Abstract

Phase composition in AlNaH_4 doped by FeCl_2 was studied by Mössbauer spectroscopy and X-ray diffraction and stabilities in Ar and air are compared. The results show that the hydride disappeared during the exposition to air. The major sodium alanate hydride is trapping gaseous impurities and transformed to the Na_2CO_3 and $\text{Al}(\text{OH})_3$.

Introduction

Alanate hydride (AlNaH_4) is an important industrial material with outstanding physical and chemical properties. AlNaH_4 can be used as a re-hydrogenated as well as an environmental friendly material. Owing to their high storage capacity and relatively low temperature of recharging, AlNaH_4 -based complex hydride have been widely applied in hydrogen tank, fuel cells, MH battery, etc. [1-3] Additives of transition metal moderate the working temperature; kinetics of dehydrogenation and do not changed the hydrogen storage capacity [1-3]. The capacity of AlNaH_4 catalyst by 5 mol. % FeCl_2 is 4.65 wt. % (1st thermolysis) and 2.13 wt. % (2nd thermolysis) [1, 2]. Thermal decomposition of this material is work at around 100°C and hydrogenation at

$120^\circ\text{C}/150$ bar of H_2 . Iron ions observed by Mössbauer spectroscopy explained role of doping $\text{Fe}(\text{OEt})_2$ which formed the nanoscales particles and transformed into Fe-Al-alloy during the re-hydrogenation steps [2]. Three types of synthesis are commonly used for the metal doping: (i) ball-milling or wet chemical reaction presynthesized metal and hydride, (ii) ball-milling of precursors under the hydrogen, (iii) the telemetrically monitored process of ball-milling, hydrogenation, and doped by metal [4].

In this paper we compare properties of dry milled AlNaH_4 and 2 mol % $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ powders in argon atmosphere and in air.

Experimental details

The complex hydride sample was mixed by dry milling of commercial pure AlNaH_4 (Alfa Aesar) and 2 mol % $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ powders in argon atmosphere and in air. After the milling in Ar the powder was sealed in a plastic bag capsule filled by Ar.

The X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) were applied for characterization of the structure of the as-prepared (before milling) powder, and after 0.5; 1 and 2.5 hours of milling in a protective (Ar) or in ambient atmospheres. XRD was carried out using X'Pert diffractometer and $\text{CoK}\alpha$ radiation with qualitative analysis by HighScore® software and the JCPDS PDF-4

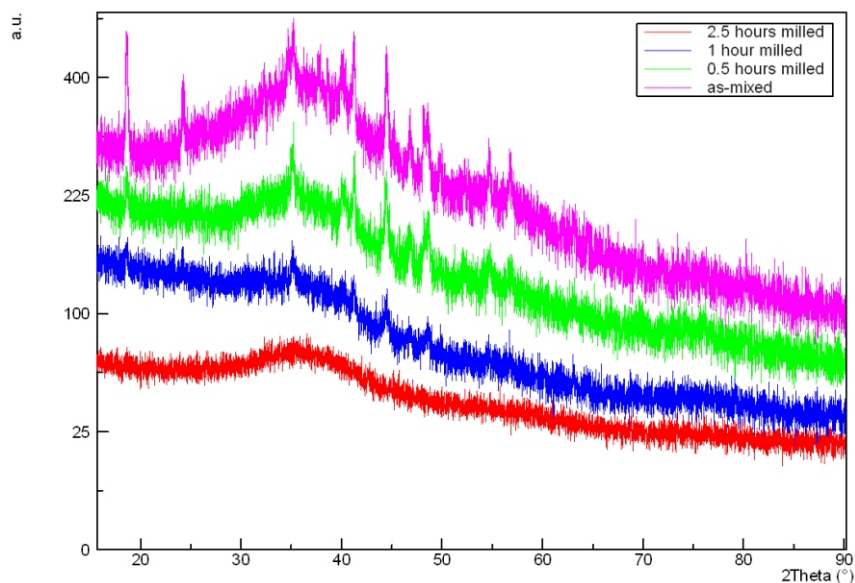


Figure 1. Comparison of XRD diffractograms of the as-mixed sample and the samples after milling in air for 0.5, 1, and 2.5 hours.

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 $^{57}\text{Co}/\text{Rh}$ source in standard transmission geometry with detection of 14.4 keV γ -rays. The velocity scale was calibrated with a standard α -iron foil at room temperature. Isomer shifts are given relative to α -Fe at room temperature. The computer processing of the spectra was done using CONFIT package [5] which yielded intensities I of the components (atomic fraction of Fe atoms), their hyperfine inductions B_{hf} , isomer shifts δ , quadrupole splittings E_{Q} , and quadrupole shifts Q .

Results

The significant differences were observed by means the MS in the sample milled in argon atmosphere and in air. Two main components can be recognized in the spectrum of the sample milled in Ar. The first component – doublet with $\delta = 1.15$ mm/s and $E_{\text{Q}} = 2.32$ mm/s – can be ascribed to FeCl_2 in agreement with [6] and the second component – doublet with $\delta = 0.31$ mm/s and $E_{\text{Q}} = 0.99$ mm/s – represents of FeOCl [7]. Different two components can be analyzed in the spectrum of the sample milled in air. The doublets have following parameters: $\delta = 0.17$ mm/s and $E_{\text{Q}} = 0.55$ mm/s and $\delta = 0.5$ mm/s and $E_{\text{Q}} = 0.63$ mm/s. These values are close to Fe(III) and Fe(III-II) in iron oxides and they probably represent paramagnetic iron bearing oxides spread in the matrix. The disappearing of the doublets of iron chloride and iron oxychloride can be explained by their further oxidation during milling and/or by a chemical reaction with sodium alanate.

XRD measurement taken in Ar does not indicate any changes in phase composition although a gas desorption was observed in the powder stored in Ar after milling by expansion of the plastic bag capsule. The diffractions of NaAlH_4 were only detected there. The XRD taken on the sample after milling in air (Fig. 1) shows formation of so-

dium carbonate Na_2CO_3 and amorphisation of remaining phases in dependence on time. Na_2CO_3 replaced sodium alanate hydride taking CO_2 from the surrounding air.

Conclusions

The exposition of AlNaH_4 doped by iron chloride to air caused changes of chemical, phase and structure composition in all steps of sample preparation. This material chemically reacts with gaseous CO_2 in ambient atmosphere and the Na_2CO_3 phase is formed. The results of MS show that the original FeCl_2 phase is oxidized and/or chemically reacts to new iron oxide phases.

References

1. T. Kiyobayashi, S. S. Srinivasan, D. Sun and C. M. Jensen, *J. Phys. Chem A* **107**, (2003), 7671.
2. B. Bogdanovic, R. A. Brand, A. Marjanovic et al., *J. Alloys Comp.* **302**, (2000) 36.
3. Tai Sun, Bo Zhou, Hui Wang, Min Zhu, *J. Alloys Comp.* **467**, (2009) 413.
4. B. Bogdanovic, M. Felderhoff, A. Pommerin et al., *J. Alloys Comp.* **471**, (2009) 383.
5. T. Žák, in *Mössbauer Spectroscopy in Materials Science*, edited by M. Miglierini and D. Petridis, (Dordrecht: Kluwer), 1999, pp. 385-386.
6. D. J. Simkin, *Phys. Rev.* **177**, (1969), 1008.
7. Yao-Dong Dai, Zhi Yu, Hong-Bo Huang, Yun He, Ting Shao, Yuan-Fu Hsia, *Mater. Chem. Phys.* **79**, (2003) 94.

Acknowledgements

This work was supported by the Czech Ministry of Education, Youth and Sports (1M6198959201), Academy of Sciences of the Czech Republic (AV0Z20410507) and Grant Agency of the Czech Republic 106/09/P556.