PREPARATION OF FE-TI COMPOSITES BY BALL MILLING

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Abstract
Although the abilities of Mössbauer spectroscopy (MS) are limited the study of the mixture of Fe-Ti powder alloy seems this method extremely valuable. The materials were prepared by mechanical alloying in the ball mill. The first type of sample consists of pure commercial precursors (TiH₂ and ferrihydride). The slightly changes of phase composition of the powder were under the detection limit of X-ray powder diffraction. The MS determined the changes from the first step of milling. The second type of sample was prepared from turnings. The reduction of the splinters volume and the mechanical alloying was running simultaneously. The huge crystalline size differences decreased the credibility of computation of phase composition by XRD. MS was able determined phase composition more exactly and in additional to differentiate crystalline and amorphous FeTi phase.

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

1. INTRODUCTION
Transition metals based composites still belong to candidates for hydrogen storage. 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].

Mechanical alloying of a Ti₄₅Zr₃₈Ni₁₇ powder mixture formed an amorphous phase, but subsequent annealing caused the formation of an icosahedral quasicrystalline phase with a small amount of the Ti₂Ni-type crystal phase [4]. After high-pressure hydrogenation at 573 K at a hydrogen pressure of 3.8 MPa, the amorphous phase transformed to a TiH₂-type hydride, while the icosahedral phase was structurally stable even after the hydrogenation.

2. EXPERIMENTAL DETAILS
The samples were prepared by dry milling in a Fritsch planetary mill (Pulverisette 7) of chemically pure precursors (TiH, FeOOH, Sigma Aldrich®) and metal splinters (material obtained from recycling of turnings) in the second case. The both type of material were prepared and manipulated in ambient atmosphere. The X-ray diffraction (XRD) and Mössbauer spectroscopy (MS) were applied for characterization of the phase composition and structure parameters of materials.

The X-ray powder patterns were collected on X’Pert diffractometer and CoKa 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 \(\gamma\) rays. The velocity scale was calibrated with a standard \(\alpha\)-iron foil at room temperature. Isomer shifts \(\delta\) are given relative to \(\alpha\)-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 \(\delta\), quadrupole splittings \(\Delta E_Q\), and quadrupole shifts \(\varepsilon_Q\).

3. RESULTS AND DISCUSSION

The analyses of precursors determine the high purity of commercial powder materials in the first case. The significant is the mean coherent size (crystalline size, MCL) computed from diffraction pattern (160 nm TiH and 50 nm FeOOH) by means Debye-Sherrer formula. The second sample was mixed from industrial recycling splinters of low carbon steel and titanium alloy. The chemical composition of metal turnings was determined by energy dispersive spectrometry (EDS) and shows 0.1 wt% C; 0.45 wt% Si; 1 wt% Mn; and 0.2 wt% S in the steel splinter and 4% Al a 4% V in the titanium splinter. The both components were milling to the smaller pieces about 2 hours.

The mixtures of precursors was milling from 0.25 till 48 hours. The changes of phase composition, lattice parameters and hyperfine interaction were observed by XRD and MS on the small amount of samples taken away from milling chamber. The X-ray patterns of the samples prepared from commercial powder show the existence of precursors at first and decreasing of particle size in dependence on the time of milling. The prolongation of time of milling up to the 12 hours indicates the decomposition of precursors and formation of magnetite, titanium oxides and pure iron. The MS clarify this process and show the decomposition of precursors from the start of milling. The variation of this phase composition should be explained of difference of sensitivity both method to the amorphous phase. While XRD determined the presence of any structure (or structures) without long range order only, the MS still recognized the atom nearest surrounding. The nucleation of solid solution of FeTi phase was recognized after 0.25 hours milling. The amount of this phase was growing up with the time of milling. The samples were extremely inhomogeneous in the first 4 hours of milling. The both of variant crystalline \((\delta = -0.15\) mm/s; \(\Delta E_Q = 0\) mm/s) [6, 7] and amorphous \((\delta = -0.2\) mm/s; \(\Delta E_Q = 0.3\) mm/s) [6, 8] FeTi phase were present. The presence of well crystalline precursors makes the analysis of amount new compound and its crystalline size impossible determine by XRD. The crystalline size is decreasing in dependence of time for the first 12 hours of milling. Extremely long time of milling (over 20 hours) cause the increasing of particle size and decomposition of the FeTi phase to the pure iron and titanium. Impurities represented iron oxides were determined by MS.

4. CONCLUSIONS

The composites created from titanium hydrides and ferrihydrides by milling comprise small particles of iron oxides and pure iron embedded in titanium oxides matrix. The powder milled from turnings contained the majority of TiFe intermetallic phase.

ACKNOWLEDGEMENT

*This work was supported by the Czech Ministry of Education, Youth and Sports (1M6198959201), Academy of Sciences of the Czech Republic (AV0Z20410507), Grant Agency of the Czech Republic (P108/11/1350) and European Regional Development Fund – (CEITEC - CZ.1.05/1.1.00/02.0068).*
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