

Mechanochemical reaction in spinel ferrite

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Mechanochemická reakcia v spinelovom ferite

Mechanicky indukované redukčné reakcie v tuhých látkach patria medzi významné mechanochemické procesy. V práci sú Mössbauerovou spektroskopiou, práškovou röntgenovou difrakciou a termickou analýzou študované zmeny vo ferite horčíka ($MgFe_2O_4$), spôsobené jeho vysokoenergetickým mletím v ocelovom mlyne. Ferit horčíka patrí medzi mäkké magnetické materiály a nachádza množstvo aplikácií v heterogénnej katalýze a v magnetických technológiách. Štruktúrny vzorec feritu horčíka môže byť prezentovaný v tvare $(Mg_{1-x}Fe_x)[Mg_xFe_{2-x}]O_4$, kde okružle zátvorky predstavujú tetraedrické (A) a hranaté zátvorky oktaedrické [B] kryštalografické polohy kationov v tesne usporiadanej aniónovej podmriežke. Označenie x reprezentuje takzvaný stupeň inverzie, ktorý je určený koncentráciou Fe^{3+} kationov v tetraedrických polohách. Ferit horčíka je čiastočne inverzným spinelom ($x = 0,91$).

Vysokoenergetický mlecí proces vedie k zmenšovaniu veľkosti kryštálov feritu horčíka do nanometrickej oblasti (~ 10 nm). Tento efekt sa prejavuje vznikom superparamagnetických komponentov v Mössbauerových spektrách mletých vzoriek. Vysokoenergetické mletie feritu horčíka vedie okrem štruktúrnych zmien aj k jeho mechanochemickej redukcii. Produktmi mechanochemickej redukcii feritu horčíka sú tuhý roztok s wüstitovou štruktúrou ($Mg_{1-x}Fe_xO$) a kovové železo (Fe). Množstvo reakčných produktov narastá s predlžujúcim sa časom mletia. Z kvantitatívnej analýzy Mössbauerových spektier vyplýva, že pomer $Fe^{2+}/(Fe^{3+} + Fe^{2+})$ narastá s predlžujúcim časom mletia z nulovej hodnoty (nemletá vzorka) na hodnotu 0,4 (vzorka mletá 20 minút).

Produkty mechanochemickej redukcii sú štruktúrne a kompozične metastabilné. Oblasť teplotnej stability reakčných produktov je v práci určená štúdiom ich odozvy na zmenu teploty v dusikovej atmosfére. Termická analýza nanokryštalických produktov mechanochemickej reakcie ukázala, že oblasť ich termickej stability je do 600 K. Pri teplotách nad 600 K dochádza k ich postupnej kryštalizácii, dokumentovanej zánikom superparamagnetických komponentov v Mössbauerových spektrách vyžihovaných vzoriek. Rast kryštálov pri ohreve mletých vzoriek je sprevádzaný kompozičnými zmenami produktov mechanochemickej redukcii. Kovové železo sa postupne oxiduje zvyškovým kyslíkom, prítomným v dusikovej atmosfére, na magnetit (Fe_3O_4). Druhý produkt mechanochemickej redukcii, tuhý roztok $Mg_{1-x}Fe_xO$, je pri ohreve v dusikovej atmosfére relatívne stabilný.

Key words: mechanochemistry, mechanochemical reduction, high-energy milling, nanocrystalline material, spinel, ferrite.

Introduction

Reduction processes induced by mechanical treatment represent an important and significant class of mechanochemical solid state reactions. Schaffer and McCormick (1989) were the first to report the mechanochemical reduction of metal oxides by a more reactive metal ($CuO + Ca \rightarrow Cu + CaO$). In subsequent publication (Schaffer, 1991), these authors have reported similar mechanochemical reduction reactions in a number of systems ($Ag_2O + Al$; $ZnO + Ca$; $ZnO + Ti$; $V_2O_5 + Ti$; $Fe_2O_3 + Ca$; $CuO + Me$, where $Me = Al, Fe, Mg, Mn, Ni$).

In ball-milling experiments involving pure α - Fe_2O_3 (Matteazzi, 1991; Kosmac, 1992; Kaczmarek, 1994; Campbell, 1995; Linderth, 1997) or mixtures of α - Fe_2O_3 and SiO_2 (Jiang, 1996) in air, reduction of α - Fe_2O_3 to Fe_3O_4 was observed to occur in a closed stainless steel container after prolonged milling.

The application of high-energy milling to the reduction of oxide spinels has been reported in only a few papers. The displacement reaction between magnetite and titanium, copper, aluminium, and zinc during mechanical treatment have been reported (Takacs, 1992). It has been found that the final products of the mechanical treatment of copper ferrite is magnetite and a spinel solid solution ($Cu_xFe_{3-x}O_4$). This indicates that the high-energy milling of the ferrite spinel generates a complex series of solid-state transformations, including mechanochemical decomposition and reduction (Goya, 1998).

In this work, we present a detailed study of the phase evolution of $MgFe_2O_4$ during high-energy milling in a stainless steel vial. Structural formula of magnesium ferrite may be written as $(Mg_{1-x}Fe_x)[Mg_xFe_{2-x}]O_4$, where round and square brackets denote cation sites of tetrahedral (A) and octahedral [B] coordination, respectively. x represents the so-called degree of inversion (defined as the fraction of the (A) sites occupied by Fe^{3+} cations). In recent work (Šepelák, 2000), we have demonstrated that high-energy milling of $MgFe_2O_4$ in ceramic-covered vials using ceramic α - Al_2O_3 balls does not lead to chemical reduction: no other phases except $MgFe_2O_4$ were detected in the milled powders. It has been found, however, that these $MgFe_2O_4$ nanoparticles are structurally and magnetically disordered due to mechanically induced cation redistribution and spin canting.

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Experimental

Polycrystalline MgFe_2O_4 was prepared by conventional solid-state reaction (further referred to as the non-activated material). The high-energy milling process was carried out in an AGO 2 planetary ball mill (Institute of Solid State Chemistry, Novosibirsk) at room temperature. The non-activated sample (10 g) was ground for various times in a hardened stainless steel vial (150 cm^3 in volume) together with hardened stainless steel balls. The ball-to-powder weight ratio was 20:1. Milling experiments were performed in air at 750 rpm.

Mössbauer measurements have been made in transmission geometry using a microcomputer-controlled spectrometer in constant acceleration mode using a $^{57}\text{Co}/\text{Rh}$ γ -ray source. The velocity scale was calibrated relative to ^{57}Fe in Rh. "Recoil" spectral analysis software (Lagarec, 1998) was used for the quantitative evaluation of the Mössbauer spectra.

X-ray diffraction (XRD) patterns were collected using a URD 6 powder diffractometer (Seifert-FPM, Freiberg) with $\text{CuK}\alpha$ radiation. The JCPDS database was utilised for phase identification. XRD patterns were analysed using the STADI P software (Stoe, Darmstadt).

Thermoanalytical measurements were performed using a SETARAM TAG 24 thermobalance with simultaneous differential thermal analysis. Samples (130 mg) were heated in open platinum crucibles up to 1100 K at a heating rate of $10\text{ K}\cdot\text{min}^{-1}$ in flowing nitrogen.

Results and Discussion

The mechanically induced evolution of MgFe_2O_4 submitted to the high-energy milling process has been followed by ^{57}Fe Mössbauer spectroscopy. Figure 1 shows the room-temperature Mössbauer spectra of non-activated MgFe_2O_4 without and with an applied magnetic field as well as the subspectra of both (A)- and [B]-site ferric ions. The Mössbauer spectrum of MgFe_2O_4 taken in zero applied magnetic field (Fig. 1(a)) indicates that there is a considerable overlap of the (A) and [B] subspectra due to the similar values, see below, taken by the hyperfine fields at the iron nuclei on the two sublattices. In the presence of an external field, the effective moments of the individual particles are to some extent aligned along the field and the resulting magnetic field at the nuclei is either enhanced or decreased by the applied field (O'Neill, 1992). In the case of MgFe_2O_4 this results in an almost complete resolution of the overlapping patterns due to octahedrally and tetrahedrally coordinated Fe^{3+} (Fig. 1(b)). The degree of inversion calculated from the subspectral area ratio of the Mössbauer spectrum without and with an applied magnetic field was found to be $x = 0.91(3)$ and $x = 0.91(7)$, respectively. The values of the hyperfine magnetic fields ($H_A = 48.16(9)\text{ T}$, $H_B = 50.01(1)\text{ T}$), the isomer shifts ($IS_A = 0.13(3)\text{ mm}\cdot\text{s}^{-1}$, $IS_B = 0.24(8)\text{ mm}\cdot\text{s}^{-1}$), and the degree of inversion are in agreement with previously published data (O'Neill, 1992).

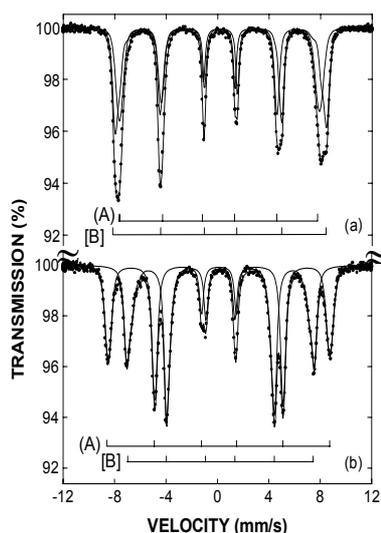


Fig. 1. Mössbauer spectrum of the non-activated MgFe_2O_4 taken in zero magnetic field (a) and in an external magnetic field of 5.5 T applied perpendicular to the γ -ray direction (b).

Obr. 1. Mössbauerové spektrum neaktivovaného MgFe_2O_4 v nulovom magnetickom poli (a) a vo vonkajšom magnetickom poli 5.5 T orientovanom kolmo k smeru γ -žiarenia (b).

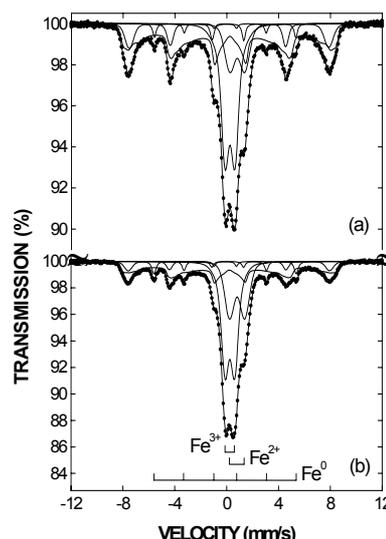


Fig. 2. Mössbauer spectra of mechanically treated MgFe_2O_4 for 10 min (a) and 20 min (b).

Obr. 2. Mössbauerové spektrum MgFe_2O_4 aktivovaného 10 min (a) a 20 min (b).

With increasing milling time, the hyperfine magnetic sextets corresponding to the tetrahedrally and octahedrally coordinated iron cations become asymmetric towards the inside of each line, slowly collapse and are gradually replaced by a central doublet with broad lines (Fig. 2). We notice that the new doublet components in the centre of the spectra are already visible after only 3 min of milling. Further milling leads to a gradual increase of their relative weights. The important observation is that the newly created central doublet is asymmetric and consist of two components assigned to Fe^{3+} and Fe^{2+} . These assignments are based on the isomer shifts of the subspectra; $IS = 0.24(9) \text{ mm}\cdot\text{s}^{-1}$ for Fe^{3+} and $IS = 0.81(8) \text{ mm}\cdot\text{s}^{-1}$ for the Fe^{2+} state (Menil, 1985). The $\text{Fe}^{2+}/(\text{Fe}^{3+}+\text{Fe}^{2+})$ ratio, calculated from the areas of both doublets, increases with increasing milling time from zero (for the non-activated sample) to about 0.4 (for the sample milled for 20 min).

To elucidate the origin of the central doublet component assigned to the Fe^{3+} ions (Fig. 2), it should be noted that the high-energy milling of MgFe_2O_4 is accompanied by the reduction of the crystallite size to the nanometer range ($\sim 10 \text{ nm}$) (Šepelák, 1998). It is well-known that the most striking effect of crystallite size reduction on Mössbauer spectra is due to superparamagnetic relaxation (Mørup, 1987). The spectral components assigned to the Fe^{3+} ions (Fig. 2) can be understood to arise from ^{57}Fe in ferrite particles with relaxation times $\tau < \tau_L$ (superparamagnetic doublet) and $\tau > \tau_L$ (slowly collapsing broadened sextets).

In addition to the disappearance of the initial magnetic sextets and the formation of both Fe^{3+} and Fe^{2+} doublet components, the mechanical treatment also leads to the formation of a new hyperfine magnetic sextet with Mössbauer parameters ($H = 34.03(4) \text{ T}$, $IS = -0.12(1) \text{ mm}\cdot\text{s}^{-1}$) characteristic of pure metallic iron (see Fig. 2). Thus, the Mössbauer data clearly show that high-energy milling of MgFe_2O_4 is accompanied by the mechanochemical reduction of Fe^{3+} cations to Fe^{2+} and to metallic iron.

To determine the phase evolution of MgFe_2O_4 during high-energy milling in greater detail, the mechanochemical reduction was also followed by X-ray powder diffraction. The XRD pattern of the non-activated sample (Fig. 3(a)) is characterised by the sharp crystalline peaks corresponding to MgFe_2O_4 (JCPDS 17-0464). During the early stages of milling, XRD reveals only a decrease of the intensity and an associated broadening of the Bragg peaks of the spinel. This reflects the formation of the disordered state with a small crystallite size and with internal strains introduced during the mechanical treatment. With increasing milling time, new diffraction lines corresponding to the solid solution $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ are formed which possesses the wüstite structure (JCPDS 35-1393). Further milling leads to a progressive mechanochemical reduction of magnesium ferrite manifested by the gradual increase in the intensities of the diffraction lines due to magnesiowüstite. The multiphase nature of the mechanically treated samples makes it impossible to determine the exact chemical composition of the solid solution. As can be seen from Fig. 3(b), in addition to $\text{Mg}_{1-x}\text{Fe}_x\text{O}$, the mechanically induced reduction process is accompanied by the formation of crystalline iron (JCPDS 06-0696). From the quantitative evaluation of the Mössbauer spectra it is concluded that the fraction of metallic iron increases with increasing milling time from 0% (for the non-activated sample) to about 5 % (for the sample milled for 20 min).

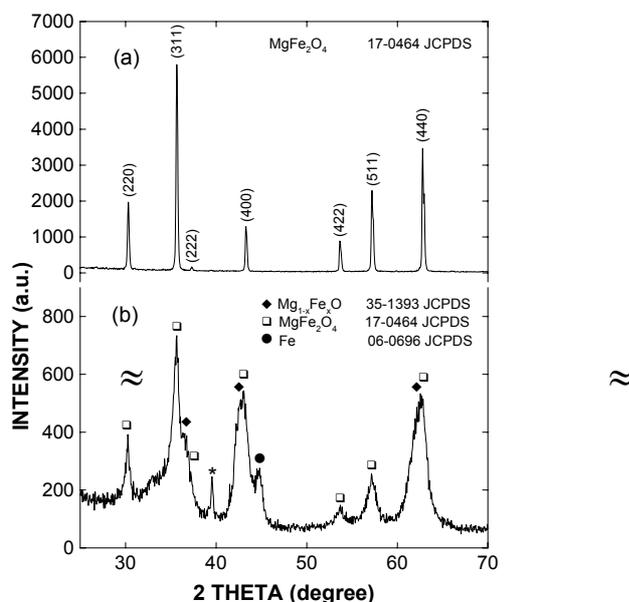


Fig. 3. X-ray diffraction patterns of non-activated MgFe_2O_4 (a) and of material mechanically treated for 20 min. * indicates a diffraction peak of the sample holder.

Obr. 3. Difrakčný záznam neaktivovaného (a) a 20 min mechanicky aktivovaného (b) MgFe_2O_4 . Symbol * označuje difrakčnú líniu odpovedajúcu podložke vzorky.

In previous work (Tkáčová, 1995), the influence of milling conditions on the contamination of powders by iron during high-energy milling has been studied. It has been found that the Fe content originating from the abrasion of the stainless steel vial and balls increases with increasing milling time. It reaches a maximum value of about 1% in the case of dry milling. It has also been shown that iron originating from the abrasion is present mainly in form of a finely dispersed powder showing superparamagnetic behaviour (Tkáčová, 1995). In contrast to this finding, the metallic iron detected in the products of the mechanochemical reduction of MgFe_2O_4 is in a magnetically ordered state, see Fig. 2. Moreover, its relatively high content provides additional evidence that it cannot be due to contamination originating from abrasion. We, thus, conclude that both the solid solution of $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ and the ferromagnetic Fe are obtained as the result of the mechanochemical reduction of MgFe_2O_4 . In this context it should be noted that the existence of a very small quantities of chromium, which originates from the abrasion of the hardened steel vial and balls (Fe18Cr8Ni), has been detected in the milled samples by electron microscopy and EDX analysis. A quantitative EDX analysis was not possible due to the small extent of the abrasion, typical for dry high-energy milling. Moreover, assuming that iron due to abrasion is in the superparamagnetic state, its contribution to the central part of the spectrum was too small to be detected by Mössbauer spectroscopy.

The spinel ferrites are known to be stable and chemically inert refractory compounds. According to the phase diagram of the system Mg-Fe-O (Becker, 1989), MgFe_2O_4 can be reduced at very low oxygen activities. For example, in a study performed at relatively low temperatures and using flowing hydrogen gas (at 720 K for 80 hours), to ensure low oxygen activities, it has been found that the reduction of MgFe_2O_4 leads to the formation of a solid solution of $\text{Mg}_{1-x}\text{Fe}_x\text{O}$ and metallic iron (Qian, 1983). Hence, under these conditions, the same reaction products are obtained that have also been observed in the case of the mechanochemical reduction of MgFe_2O_4 performed at room temperature and in air. The mechanically induced reduction of MgFe_2O_4 , thus, demonstrates that mechanical treatment offers an alternative route to the conventional thermally activated reduction processes.

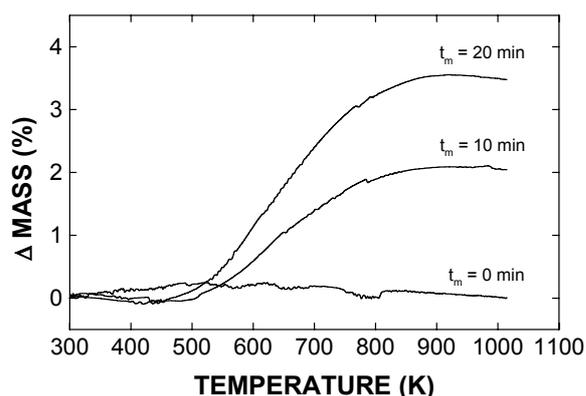


Fig.4. Thermogravimetric curves of MgFe_2O_4 mechanically treated for various times (t_m).
Obr.4. Termogravimetrické krivky mechanicky aktivovaného MgFe_2O_4 (t_m - čas aktivácie).

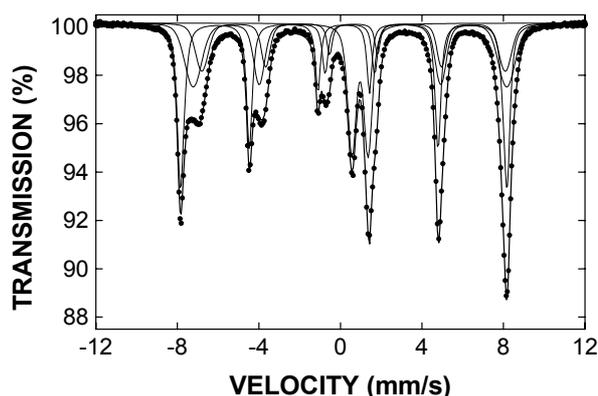


Fig.5. Mössbauer spectrum of mechanically treated (20 min) MgFe_2O_4 after annealing at 1000 K in nitrogen atmosphere.
Obr.5. Mössbauerové spektrum mechanicky aktivovaného (20 min) MgFe_2O_4 po vyžihani pri 1000 K v dusikovej atmosfére.

The products of the mechanochemical reduction reaction are metastable with respect to structural and compositional changes under temperature and environmental conditions. Information on the structural response of the mechanochemical reduction products to changes in temperature was obtained by thermogravimetric measurements (TG) performed in a nitrogen atmosphere. While the thermal treatment of the non-activated sample does not produce any weight changes, the heating of the milled samples is accompanied by an increase in weight due to the oxidation of the reduction products by the residual oxygen in the nitrogen atmosphere (Fig. 4). However, assuming that during heating only the oxidation of metallic iron to magnetite ($3\text{Fe} + 2\text{O}_2 \rightarrow \text{Fe}_3\text{O}_4$) takes place, the mass increase should be lower than that actually determined by TG. In the case of the sample activated for 20 min, e.g., the mass increase should be about 1.5% lower than that determined by TG ($\sim 3.5\%$). This indicates that in addition to metallic iron, also a partial oxidation of the solid solution takes place during heating. Partial oxidation of the solid solution was confirmed by Mössbauer spectroscopy of the annealed samples. The Mössbauer spectrum of the sample milled for 20 min after annealing at 1000 K (Fig. 5) shows the overlapping sextets (corresponding to magnetically ordered magnesium ferrite and magnetite) and the paramagnetic doublet characteristic of Fe^{2+} cations in the solid solution (Goldanskii, 1968),

while the superparamagnetic components vanished due to recrystallisation process. The quantitative evaluation of the Mössbauer spectra shows that the thermal treatment of the milled samples results in a decrease of the Fe²⁺ content in the solid solution by about 5% when compared with the sample before annealing. Thus, the thermally induced structural evolution of the milled samples is also accompanied by the partial oxidation of the solid Mg_{1-x}Fe_xO solution.

Conclusions

The changes in MgFe₂O₄ induced by high-energy milling in a stainless steel vial have been investigated by Mössbauer spectroscopy, X-ray diffraction, and thermal analysis. In addition to the formation of nanoscale ferrite particles, the mechanical treatment results in the mechanochemical reduction of MgFe₂O₄ to a solid solution Mg_{1-x}Fe_xO and Fe. The fraction of the reaction products increases with increasing milling time. The nanocrystalline products of the mechanochemical reduction are metastable with respect to structural and compositional changes at elevated temperature. In nitrogen atmosphere, the range of the thermal stability of the nanoscale products extends up to 600 K. At temperatures above 600 K the nanoscale products gradually begin to crystallise. This is accompanied by the oxidation of the metallic iron to Fe₃O₄, while the solid solution is chemically relatively stable with respect to temperature.

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