X-ray Diffraction Analysis by Williamson-Hall Method of Strontium Hexaferrite Lattice Features after Mechanical Milling

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Abstract. The paper presents the result of experimental studies of strontium hexaferrite milling in beater mill. SEM studies showed that milling of strontium hexaferrite in beater mill with formation of magneto fluidized bed leads to significant intensification of the process. Williamson-Hall method was used to determine structural characteristics changes in the strontium hexaferrite powder from milling time in magneto fluidized bed. Carried out studies showed that milling intensification is significant only to a certain dispersity of processed powder. However, during milling with formation of magneto fluidized bed, decrease of particle sizes and structural characteristics changes speed happens at finer disperse compound.

1. Introduction

Application of ferromagnetic powders in powder metallurgy makes high demands not only to powder disperse compound but also to its structural characteristics. Mechanical milling is often applied to produce powders of defined dispersity. In order to reduce sizes of initial material particles one use various kinds of ball, beater, planetary, jet mills [1-3]. In most cases the problem is not only to obtain fine powder, but to do it with minimal time and energy consumption. This leads to necessity of development of rational milling methods [4-5].

Milling process of ferromagnetic materials can be intensified by fluidized bed [6], created by rotatory magnetic field [7] or by perpendicular alternating gradient and constant magnetic fields [8]. Milling of coarse ferromagnetic materials in beater mill with application of alternating gradient and constant magnetic fields with mutually perpendicular induction lines provides more intense milling of powder than just milling in beater mill. Due to significant reduce of milling time with magneto fluidized bed, obtaining powder of defined dispersity becomes more energy effective [9]. Impact actions that effect powder particles in beater mill change sizes of structural elements and increase lattice micro strain level. However, during milling in beater mill with magneto fluidized bed, the speed of structural characteristics changes increases due to self-milling caused by impacts between particles [10]. For this reason, studies of state of structural powder characteristics are an important task when optimizing powder processing conditions. Presently the methods of X-ray diffraction (XRD) analysis are widely and effectively used in studies of structural characteristics of particulate materials [11].
The goal of current work was to establish patterns of changes of strontium hexaferrite structural characteristics ($\text{SrFe}_12\text{O}_{19}$) during milling in beater mill with formation of magneto fluidized bed by means of X-ray diffraction and Williamson-Hall method.

2. Experiment
Coarse strontium ferrite with average particle size 1558.5 µm and 1476.9 particle median size was milled in beater mill by rotating with 15 krpm beaters. Constant and alternating magnetic fields with mutually perpendicular induction lines effected on milled material to form magneto fluidized bed. Induction of constant one was 15.3 mT and alternating one had 90 mT/m gradient and 50 Hz frequency. Analysis of particle size distribution was carried out by SEM Ziess Supra 25. Structural characteristics of particulate material were studied by X-ray diffraction method on Shimadzu XRD – 7000 diffractometer with CuKα emitting anode with 1.5406 Å wavelength with Bregg-Brentano focusing ($\theta$–2$\theta$). Diffraction peaks were analyzed using PowderCell 2.3 [12] based on full profile Rietveld refinement method [13]. Diffraction studies were carried out at room temperature in step scan mode (0,03° step) covering 2θ interval from $5^\circ$ to $90^\circ$.

One important task of powder materials structural characteristics studies is obtaining results that describe structural state in the best way. In order to get coherent scattering regions (CSR) sizes and values of micro strain, one widely uses various XRD methods [14-16].

3. Results and discussion
During milling in magneto fluidized bed ferromagnetic particle is effected by a pair of forces trying to turn its magnetic moment in the field’s direction and a moving force with value proportional to magnetic field induction gradient. Particles do translational motion with frequent abrupt change of speed by direction. Such motion leads to holding of powder in the area of rotating beaters and increase number of interparticle collisions intensifying milling process and affecting structural characteristics of particles. Milling intensification is proved by SEM studies of particle size distributions dependencies from milling time. Dependencies of strontium hexaferrite average particle sizes and median values from milling time without electromagnetic effect and with magneto fluidized bed are presented on Figure 1. Milling just by rotating beaters for 30 minutes provides decrease of average particle size to 13.9 µm and median to 9.6 µm (Figure 1 a, c). After 120 minutes milling average particle size and median became 9.2 µm and 6.4 µm correspondingly. Milling with formation of magneto fluidized bed with 90 mT/m induction gradient of the alternating magnetic field during 30 minutes gave average particle size 2.3 µm and median 1.6 µm (Figure 1 b, d). After 120 minutes average particle size became 0.57 µm and median 0.46 µm.

So, after 30 minutes milling without electromagnetic effect average particle size decreased in 112 times and with magneto fluidized bed – in 677 times. Figure 1 shows that further milling in both regimes goes with decreased intensity.

![Figure 1. Dependency of strontium hexaferrite powder average particle size and median value from milling time without electromagnetic field (a, c) and in magneto fluidized bed formed by alternating magnetic field with 90 mT/m induction gradient (b, d).]
Magneto fluidization of particulate system during milling process significantly effects on powder structural characteristics. Analysis of diffraction peaks widening allows determination of CSR sizes and lattice micro strain \( \epsilon = \Delta d/d_{hkl} \), where \( \Delta d \) is average change of interplanar distance \( d_{hkl} \) caused by lattice defects. Diffractogram fragments of initial strontium hexaferrite and after milling during 10, 30 and 120 minutes are presented on Figure 2. These XRD peaks widens as milling time increases. Such widening can be caused by both lattice microstrain and changes of CSR sizes. Williamson-Hall method allows to separate CSR sizes and micro strain contributions to peak widening [17–21]. 30 peaks with relative intensity more than 5% were taken for analysis.

Figure 2. Fragment of relative intensity diffractograms of particulate strontium hexaferrite: initial (a), milled in magneto fluidized bed with 90 mT/m induction gradient for 10 minutes (b), 30 minutes (c) and 120 minutes (d).

The biggest and the smallest values of CSR sizes \( D \) and lattice micro strain \( \epsilon \) can be obtained when approximating peaks with Lorentz and Gauss functions. In case of Lorentz approximation, full peak widening consists of size (CSR) and strain \( \epsilon \) widening factors \( \beta = \beta_{\text{size}} + \beta_{\text{strain}} \). In case of Gauss approximation \( \beta^2 = \beta_{\text{size}}^2 + \beta_{\text{strain}}^2 \).

The equations have the following form:

for the case of Lorentz approximation

\[
\beta = \left( \frac{\lambda}{D \cos(\theta)} \right) + \left( 4\epsilon \cdot \cot(\theta) \right)
\]  

(1)

for Gauss approximation

\[
\beta^2 = \left( \frac{\lambda}{D \cos(\theta)} \right)^2 + \left( 4\epsilon \cdot \cot(\theta) \right)^2
\]  

(2)

If experimental peak is approximated by Lorentz function, the dependency of \( \beta \cos \theta \) from \( 4\sin \theta \) is plotted (Figure 3); in case of Gauss approximation \( \beta \cos \theta \) from \( 4\sin \theta \) (Figure 4). Plotted data is fitted by a line equation. In Lorentz case (1) line slope gives \( 4\epsilon \) and intercept \( -\lambda/D \). In Gauss case (2)
slope corresponds to \((4\varepsilon)^2\) and intercept to \((\lambda/D)^2\). Slope gives information about lattice strain \(\varepsilon\) and intercept provides CSR size \(D\) and dislocation density \(\rho = 3(D)^{1/2}\).

**Figure 3.** Plots of \(\beta\cos(\theta)\) from \(4\sin(\theta)\) for Lorentz approximation of initial strontium hexaferrite powder diffraction peaks.

**Figure 4.** Plots of \(\beta^2\cos^2(\theta)\) or \((4\sin(\theta))^2\) for Gauss approximation of initial strontium hexaferrite powder diffraction peaks.

By analysis of Lorentz and Gauss diffraction peaks approximations on Figure 3 and 4, we found out minimal and maximal values of structural parameters, their average and scatter:

\[
\frac{\Delta d}{d} = 0.001541 \pm 0.000275; \quad (17.8 \%); \quad (1) 
\]

\[
D = (360.91 \pm 4.08) \text{ Å} ; \quad (1.1 \%); \quad (2) 
\]

\[
\rho = (2.3040 \pm 0.0520) \times 10^{-5} \text{ Å}^2 ; \quad (2.2 \%); \quad (3) 
\]

By the same Willamson-Hall method we found out minimal, maximal and average values of \(D\), \(\varepsilon\) and \(\rho\) for powders obtained by milling in beater mill with magneto fluidized bed. Dependencies of lattice strain \(\varepsilon = \Delta d/d\), CSR size \(D\) and dislocation density \(\rho\) from milling time are presented on Figure 5, 6 and 7 for strontium hexaferrite milled with effect of alternating magnetic field with 90 mT/m gradient.

**Figure 5.** Dependencies of lattice strain from time of milling of initial strontium hexaferrite in beater mill: Lorentz approximation (a), Gauss approximation (b), average (c).
Figure 6. Dependencies of CSR size $D$ from time of milling of initial strontium hexaferrite in beater mill: Lorentz approximation (a), Gauss approximation (b), average (c).

Figure 7. Dependencies of dislocation density $\rho$ from time of milling of initial strontium hexaferrite in beater mill: Lorentz approximation (a), Gauss approximation (b), average (c).

Processing of initial particulate medium with magneto fluidized bed during 10 minutes leads to increase of average $\Delta d/d$ from 0.00035 to 0.00045 (Figure 5), $D$ decreased from 310 to 300 Å (Figure 6) and value of $\rho$ increased from $3.13 \cdot 10^{-5}$ Å$^{-2}$ to $3.34 \cdot 10^{-5}$ Å$^{-2}$ (Figure 7). Subsequent 20 minutes milling gave increase of $\Delta d/d$ to 0.00121, decrease of $D$ to 267 Å and increase of $\rho$ to $4.16 \cdot 10^{-5}$ Å$^{-2}$. Further, milling with magneto fluidized bed from 30 to 120 minutes changed $\Delta d/d$ to 0.00133 (9.9% vs 245.0% in first 30 minutes), $D$ to 252 Å (5.6% vs 13.8%) and $\rho$ to $4.70 \cdot 10^{-5}$ Å$^{-2}$ (13% vs 32.9%). So, after 30 minutes (when average size is several micrometers), speed of change of structural characteristics decreases with powder particle sizes.

4. Conclusion

Application of magneto fluidized bed to milling of strontium hexaferrite in beater mill provides process intensification and obtaining of submicron powder in 120 minutes. The speed of change of structural characteristic depends not only from intensity of milling process, but also from size of powder particles greatly decreasing with their smaller sizes.
5. References

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