Investigation of typical properties of nanocrystalline iron powders prepared by ball milling techniques

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Abstract

Metallic powder has applications in many fields. In applications for preservation and anti-oxidation, iron powder has been used as an air oxygen reducer which is capable of decreasing microclimatic oxygen concentrations in a hermetic mini-environment. In this role, if we increase the specific surface area by reducing the particle size of the iron powder, the rate and performance of oxygen reduction will be improved significantly. In addition, the porosity of iron powder also contributes considerably. The iron powder can be fabricated using many methods: chemical deposition, powder metallurgy and mechanical milling. The technique of milling has certain advantages, especially for the formation of technical iron powder. The experimental equipment used was a Fritsch P-6 planetary ball mill. The iron powder was prepared with different milling times, from 1 up to 30 h in acetone as a protective environment. The powder products obtained were analyzed using field emission scanning electron microscope (FE-SEM), energy dispersive x-ray (EDX), x-ray diffraction (XRD), dynamic laser scattering (DLS), Brunauer–Emmett–Teller (BET) techniques and also magnetic characterization by vibrating sample magnetometer (VSM). The results show a correlation between the milling time and the crystallite and particle size, specific surface area, magnetic properties and nanoscale porosity of the iron powder. The iron powders obtained were a kind of mesoporous materials. The properties of the iron powder were examined with respect to their oxygen reducing kinetics.

Keywords: iron powder, ball milling technique, nanocrystalline size, specific surface area, saturation magnetization

Classification numbers: 4.00, 4.03, 5.00, 5.02, 5.18

1. Introduction

Metal powders have been used in many fields and have an important role in equipment manufacture using sintering techniques [1, 2]. In addition, some active metal powders such as zinc and iron powders, being easily oxidized in natural atmosphere, have been also used as air oxygen reducers decreasing air oxygen concentrations in a hermetic mini-environment for anti-oxidation preservation [3, 4].

Among metal powders, iron powder has been the most manufactured and used. Nanoscale iron particles represent a new generation of environmental remediation
technologies that could provide cost-effective solutions to some of the most challenging environmental cleanup problems. Nanoscale iron particles have large surface areas and high surface reactivity. Equally important, they provide enormous flexibility for in situ applications. Research has shown that nanoscale iron particles are very effective for the transformation and detoxification of a wide variety of common environmental contaminants, such as chlorinated organic solvents, organochlorine pesticides and polychlorinated biphenyls (PCBs). Modified iron nanoparticles, such as catalyzed and supported nanoparticles have been synthesized to further enhance the speed and efficiency of remediation [5].

There are many methods to manufacture iron powder, such as mechanical grinding, spraying the molten metal under high pressure into a rapidly cooled environment, reconstituting oxide powders using CO, pyrolysis of metallic carbonyl compounds, electrochemical deposition, etc. The technique of mechanical grinding has been considered as it possesses certain advantages, especially for manufacturing a technical iron powder.

High-energy milling method has usually been used to fabricate powder materials with a few tens of nanometers in size. The material milling is based on the impact of the hard steel balls which rotate in a closed chamber with a very high speed. A sealed chamber containing materials for milling can be kept in a high vacuum condition or filled by a noble gas or liquid as a protective environment. The milling with balls made from hard alloy steel or hard materials such as tungsten carbide and plastic polyamide [7]. Vials and grinding balls used in this study were fabricated from tungsten carbide.

The milling process of manufacturing iron powder is described in scheme 1. The raw material for the Fritsch P-6 planetary ball mill was coarse iron powder prepared by the electrochemical deposition method [8]. The average particle size was 160 µm, particle shape is uniform, the morphology was observed by FE-SEM (figure 2(a)), purity >97.4% (table 2). The ball-to-powder weight ratio was 10:1 [7]. In order to minimize oxidation, the milling operation was performed in anhydrous acetone which was filled in the vials before milling. The samples were crushed with a setting of P6.1 mode (speed 500 rpm, each cycle time: 15 min of milling, 5 min of standing). The steps are shown in scheme 1. After a certain period of milling, the mixed product of each batch was removed from the vials and the protecting solvent was separated in the absence of oxygen. Then, the iron powder was dried in vacuum at room temperature, about 40–50 °C for 30 min, following a package for the preservation in a hermetic micro-environment in very low oxygen concentration.

Studied iron powder samples are listed in table 1, in which the sample N0 is the initial material. The composition and structure of the samples were examined on the XRD, model SIEMENS D5000; surface morphology and chemical composition were determined by FE-SEM and EDX, model FESEM S-4800. Particle size distribution was determined by DLS on the HORIBA LA-950 equipment. The specific surface area and the pore size distribution were determined

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**Table 1.** Symbol and input parameters for the Fritsch P-6 planetary ball mill, milling mode P6.1.

| Sample | N0 | N1 | N2 | N3 | N4 | N5 | N6 |
|--------|----|----|----|----|----|----|----|
| Weight (g batch⁻¹ vial⁻¹) | 15.01 | 15.02 | 15.02 | 15.01 | 15.02 | 15.01 | 15.02 |
| Milling time (h) | 0 | 1 | 2 | 5 | 10 | 20 | 30 |

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**Scheme 1.** Steps in the mechanical grinding process to prepare fine iron powders.
using the method of isothermal adsorption of nitrogen on the ASAP 2020 V3.01H. Several magnetic properties of milled iron powder such as saturation $M_s$ and coercivity $H_c$ were determined using the magnetization curves $M(H)$ [9] measured by VSM, DMS 880 model at room temperature.

The crystallite size was calculated from the XRD pattern using the Scherrer’s equation [10]

$$D_{crys} = \frac{k\lambda}{\beta \cos \theta},$$

where $D_{crys}$ is crystal size (nm), $\theta$ is peak angle, $\lambda$ is the x-ray radiation wavelength ($\lambda = 0.154056$ nm for Cu-Kα cathode), $\beta$ is the width of the XRD peak at half height (radian) and $k$ is a shape factor (about 0.89 for magnetite and maghemite). $2\theta = 44.67^\circ$ is the position of the maximum diffraction peak corresponding to the (110) plane.

The particle sizes of the powders ($D_{BET}$) were determined using the Brunauer–Emmett–Teller (BET) method and equation [11]

$$D_{BET} = \frac{6}{\rho S_i},$$

where $\rho$ is the density ($g m^{-3}$) and $S_i$ is the specific surface area of the iron powders ($m^2 g^{-1}$).

### 3. Results and discussion

#### 3.1. The composition and crystal structure

Raw materials and grinding products were analyzed to determine their components (iron metal/iron oxides) by EDX analysis. The results showed that with milling time of the range from 1 to 30 h, the products’ purity (iron metal) is very high, up to 97%.

Table 2 presents obtained results of the analysis, N0 sample—without milling, N6 sample—30 h milling. The average values of the percentage by weight show an increase of the impurity (iron oxides) component, but it is very small. A total purity difference of N6 sample compared to the original sample N0 was only 0.70% in mass, which means there was nearly no oxidation occurring during the preparing process.

The EDX spectra of the N0 and N6 samples are shown in figure 1(a) (without milling) and 1(b) (30 h milling). This result shows that there is no change between the EDX spectra even through increasing milling time up to 30 h. The grinding process, as well as the processing and storage of the product did not generate any new peak in the EDX spectrum, in comparison with raw materials; in particular, the percentage of oxygen is nearly not increased.

The observation results obtained by FE-SEM showed that in the early stages of the milling process, the iron powder particles were flattened to form thin plates with small thickness, but their surface areas were large (figure 2(b)). When the milling time was less than 5 h, the particles reached sizes of a few tens of micrometers.

When the milling time was increased to more than 5 h, the observation on FE-SEM image shows the presence of a significant amount of individual particles 50–85 nm in size (figure 3(a)), but they mostly linked to form particle clusters a few micrometers in size (figure 3(b)). While the milling time was continuously increased to 10 h and more, the results of measuring the size distribution by DLS technique show that the average sizes of the clusters decreases significantly, as shown in figure 8(a).

When milling time was increased from 1 to 30 h, the XRD diagram, with angle 2$\theta$ values in the range from 20° to 100° of all samples from N0 to N6 have four characteristic diffraction peaks of crystalline iron of BCC $\alpha$-Fe structure. However, the width of the peaks tended to be broader, and the peak intensity decreased with increasing milling time, and small amounts of debris appeared on the peaks. An x-ray diffraction diagram of the N1, N3, N5 and N6 samples is shown in figure 4(a).

Based on equation (1), the crystalline size $D_{crys}$ of iron powders was determined as a function of the milling time, as shown in figure 5. In the early stages of the milling process, the crystalline size decreased, however, with increasing milling time more than 5 h, the size also decreased but very slowly (figure 5). From this it can be understood that the balls’ impact on the small particles decreased strongly in comparison with that on big particles, and the long milling time would approach the critical parameter of the machine.

X-ray diffraction diagrams (figure 6) did not show any new phase which suggests that this milling process is effective at protecting the metal iron powder from oxidation. This result was entirely consistent with published data [12, 13].

#### 3.2. The particle size distribution

The particle size distributions of the samples N1–N6 and the original iron powder N0 sample (raw materials) were analysed by DLS technique. The results show a very strong shift of the particle size distribution curves as a function of milling time, and especially the peaks become narrower (figure 6).

The results also show that the particle size of sample N0 is nearly no oxidation occurring during the preparing process. When milling time was increased to more than 5 h, the observation on FE-SEM image shows the presence of a significant amount of individual particles 50–85 nm in size (figure 3(a)), but they mostly linked to form particle clusters a few micrometers in size (figure 3(b)). While the milling time was continuously increased to 10 h and more, the results of measuring the size distribution by DLS technique show that the average sizes of the clusters decreases significantly, as shown in figure 8(a).

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#### Table 2. Chemical components of N0 and N6 sample, achieved from EDX results.

| Element | O (wt%) | Fe (wt%) | Total (wt%) |
|---------|--------|---------|------------|
|         | N0     | N6      | N0         | N6         |
| 1       | 1.91   | 3.12    | 98.09      | 96.88      | 100        | 100        |
| 2       | 2.41   | 2.90    | 97.59      | 97.10      | 100        | 100        |
| 3       | 2.59   | 2.98    | 97.41      | 97.02      | 100        | 100        |

Figure 1. The EDX spectra of the iron powder: (a) without milling and (b) after 30 h milling.
Figure 2. Morphology of samples: N0 (a), N1 (b).

Figure 3. Morphology of iron powder N4: individual particles (a), clusters (b) of iron powder.

Figure 4. X-ray diffraction patterns of samples: (a) N1, N3, N5, N6 and (b) N0–N6: two peaks at $2\theta = 44.67^\circ$ and $82.32^\circ$ corresponding to the planes (110) and (211).

only in the range of 1–30 $\mu$m, meaning that the width of peaks becomes about ten times smaller (figure 6).

Based on the particle size distribution, the average sizes of particle $D_{DLS}$ were determined. The specific surface area $S_s$ of product iron powder was determined using isothermal nitrogen adsorption method. The plots of average size $D_{DLS}$ and $S_s$ area versus milling time are shown in figure 7 (curves a and c). When milling times increased up to 30h, $D_{DLS}$ reduced from 160.77 down to 7.21 $\mu$m, and the specific surface area increased from approximately 1 to 7 $m^2 g^{-1}$. 

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It is empirically found that the average particle size depends on milling time according to equation

\[ D_{\text{DLS}} = 2.97 \exp \left( \frac{25}{t + 6.27} \right) \]  \hspace{1cm} (3)

where \( D_{\text{DLS}} \) is the average size (\( \mu m \)), \( t \) is the milling time (h). Correlation coefficient of the empirical equation (3) is very high, reaching 0.999.

The obtained empirical equation describes well the general decline of particle size as a function of milling time, in the range of 1–30 h (curves a and b in figure 7). Extrapolating the milling time up to 100 h, the obtained product should reach an average particle size \( D_{\text{DLS}} = 3.76 \mu m \). According to the FE-SEM observation there are iron nanoparticles. But results of DLS technique show the average size in micrometers, meaning the size of particle clusters. These clusters can also be practically observed in the FE-SEM images (figure 3).

The value of the maximum distribution \( P_{\text{max}} \) and particle size \( D_{\text{Pmax}} \) at the maximum distribution of the iron powders took a strong variation in the first 5 h of milling, then the variation of these parameters slowly decreased (figure 8). The results indicate that the range of 1–5 h is the period of milling for the strongest particle size reduction. After the first 5 h of milling, the average particle size of the powder products reduced from 160 down to 25 \( \mu m \) and after 10 h of milling time, the size dropped below 10 \( \mu m \).

While the milling times increased above 5 h, average particle sizes changed slightly, but the specific surface area continuously increased (curve c in figure 7). These results supported that the images of the nanoparticles and the clusters including the other nanoparticles were very reliably observed by FE-SEM (figure 3). Therefore, it can be confirmed that the particle sizes measured by DLS were the size of the independent clusters.

### 3.3. Specific surface and porosity

For the sample with 5 h of milling, the \( S_{\text{pore}}/S_s \) ratio changes slightly and takes a value of about 10–20%, which means that the surface of porosity contributes about 10–20% of the total specific surface area of the powder, while the specific surface area continues to increase strongly with increasing milling time (figure 9). Therefore, it is demonstrated that an amount of new particles is continuously generated when milling time is increased up to 20 h. But, after 20 h of milling, the specific surface area and average micropore diameters have a little variation, at this time the maximum distribution \( P_{\text{max}} \) increased, which means that more and more uniform particle sizes of product powders were formed. Thus, it can be seen that the first stage of the grinding process produces the greatest deformation of the raw material with cracks appearing due to the mechanical effect of the mill balls and the particles’ own many corners and edges.

With increasing specific surface area from 1.2 to 7.3 \( \text{m}^2\text{g}^{-1} \), the average diameter of micropores also increases from 15 to 70 nm. This result shows that the obtained iron powder is of mesoporous materials.

The dependence of the porosity on milling time is shown in figure 10. After 1 h of milling, average micropore diameters
increased strongly in comparison with raw materials. However, when the milling time continues increasing, the diameters tend to decrease. This means the micropores’ specific surface area slightly depends on the milling time, even up to 30 h. With 5 h of milling, flat particles are created (see figure 2(b)) because of the plastic deformation. Then they are broken up to increase the number of grains, and porosity increases providing the strong increase of micropores’ specific surface area, thus the total specific surface area consequently increases (figure 9).

Correlation between the milling time and particle size is described according to equation (3). Therefore, it can be said that particle size reduction process is stable and balanced with the process of recombination between nanoparticles together to form clusters after 20 h of milling, as mentioned above.

The particle sizes of N3–N6 samples are at nanometer scale, and thus sizes \(D_{\text{BET}}\) are determined by BET method using specific surface area \(S_t\) based on equation (2). The results show that \(D_{\text{BET}}\) decreased, and specific surface area \(S_t\) evidently increased, shown in figure 11.

The general results of the study are listed in table 3 which shows the main characteristics of the milled iron powder samples for different milling times.

3.4. Magnetic properties

The magnetization curves \(M(H)\) were measured at room temperature using VSM type DMS 880, with the applied external field \(H\) from \(-11\) to \(+11\) kOe. The growth rate of \(H\) in each step was 180 Oe in staying 3 s, but in the range of \(-500\) to \(+500\) Oe, the step was 100 Oe. All of the iron powder samples before and after milling provided the same type of characteristic magnetization curves, as shown in figure 12.

The parameters such as saturation magnetization \(M_s\) and coercivity \(H_c\) were determined from the magnetization curves \(M(H)\). The results were summarized in table 3.

Figure 9. Effect of milling time on specific surface area \((S_s)\), \(S_{\text{po}}\) to \(S_t\) ratio of the iron powder \((S_{\text{po}}/S_t)\).

Figure 10. Effect of milling time on average micropore diameters \((D_{\text{po}})\) and specific micropores volume \((V_{\text{po}})\).

Figure 11. Effect of milling time on average particle size \((D_{\text{BET}})\) and specific surface area \((S_s)\).

\[
M_s = 200.83 - 2.01t, \quad (4)
\]

where \(M_s\) is the saturation magnetization (emu g\(^{-1}\)), \(t\) is the milling time (h). Linear fitting correlation coefficient \(R\) of relation between \(M_s\) and \(t\) is relatively high, \(R = 0.981\). This is a testament to the high linearity and reliability of the results.

Figure 12 shows the dependence of saturation magnetization \(M_s\) on the crystal size \(D_{\text{cryst}}\) and the average cluster size \(D_{\text{DLS}}\) of the iron powder samples. Accordingly, when the milling time was increased, these sizes and \(M_s\) decreased. At the first stage of the milling process, reduction of \(M_s\) was smaller than the reduction of the particle sizes.

After 5 h of milling, the particle size decreased slowly but conversely \(M_s\) decreased rapidly; especially \(M_s\) decreased strongly depending on \(D_{\text{DLS}}\) (figure 14). The decrease of \(M_s\) can be caused by the effect of decrease of particle size and surface energy consumption during the milling process. There was a formation of amorphous phase on the surface of the iron powder particles, because the intensity of diffraction peaks in XRD schema decreased with increasing milling time. On the other hand, the intensity of peaks and \(M_s\) increased again approximately back to the original value, after incubating at \(350\) °C for \(2\) h in an argon atmosphere. It can be considered as a form of clusters.

In conclusion, in addition to observing by FE-SEM, x-ray diffraction spectrum and the changes of specific surface area, the variations of the saturation magnetization gives us evidence of forming nanoparticles of iron metal powder after 5 h milling.

The relationship between the variation of coercivity of the powder product and crystal size is also shown in figure 14 (line \(H_c(D_{\text{cryst}})\)). The results showed that \(H_c\) increased when \(D_{\text{cryst}}\) decreased, corresponding to the increase of milling time. Iron is a kind of soft magnetic material which has a weak anisotropy; coercivity is proportional to the anisotropy of the crystal [14]. The increase of \(H_c\) corresponding to decrease of
Table 3. Summary of results of analysis of the typical properties of the iron powder samples.

| Sample | N0  | N1  | N2  | N3  | N4  | N5  | N6  |
|--------|-----|-----|-----|-----|-----|-----|-----|
| Purity (wt%) | 97.70 | 97.49 | 97.36 | 97.21 | 97.10 | 97.02 | 97.00 |
| Average cluster size | 160.77 | 90.86 | 64.07 | 26.05 | 11.69 | 8.89 | 7.23 |
| BET particle size | – | – | – | 245.81 | 177.21 | 107.32 | 104.38 |
| Crystal size | 40.37 | 26.07 | 22.62 | 2.9 | 4.3 | 7.1 | 7.3 |
| Specific surface area | 1.2 | 2.1 | 3.1 | 245.81 | 177.21 | 107.32 | 104.38 |
| Average micropore diameter | – | – | – | 245.81 | 177.21 | 107.32 | 104.38 |
| Saturation magnetization | 206.83 | 200.52 | 194.22 | 188.89 | 178.44 | 154.22 | 145.98 |
| Coercivity | 35.18 | 40.33 | 50.01 | 49.57 | – | 57.87 | 61.57 |

Figure 12. The magnetization curves \(M(H)\) of samples N1, N4 and N6.

Figure 13. Effect of milling time on saturation magnetization \(M_s\) of the iron powder samples.

Figure 14. The variation of saturation magnetization corresponding to the average cluster size \(M_s(D_{DLS})\), crystallite size \(M_s(D_{crys})\) and \(H_c(D_{crys})\).

To show the dependence of the variation in grinding products’ coercivity on the crystal size, correlation function between \(H_c\) and \(D_{crys}\) was fitted with the experimental data. The fitting obtained was a linear function as follows:

\[
H_c = 65.24 - 0.79D_{crys}, \quad (5)
\]

where \(H_c\) was the coercivity of milled powder product (Oe), \(D_{crys}\) was the crystal size (nm). Linear fitting correlation coefficient \(R_1\) of relation between \(H_c\) and \(D_{crys}\) was high, reaching \(R_1 = 0.953\).

4. Conclusions

Iron powders were prepared using mechanical milling on the Fritsch P-6 planetary ball mill, with milling times in the range of 1–30 h. The iron powders obtained have the following typical characteristics:

- Morphology, crystal structure, particle size, porosity and saturation magnetization, coercivity change over milling time. When the time increases, the particle size and the saturation magnetization decrease, but the coercivity increases.
- The crystal structure of BCC \(\alpha\)-Fe did not change during the milling process. Iron powder products obtained possess high purity >97%. The increase of the impurity component is very small, in total 0.70%.
Iron powder components were maintained as similar to the raw material’s components. No new crystalline phases appeared in iron powder products, especially without iron oxide phases.

- The specific surface area of iron powder products increased seven times, while the average micropore diameter reduced down from 70 nm and achieved stability at 20 nm approximately, for 30 h of milling. The iron powders obtained were a kind of mesoporous materials. The porous surface area contributed over 10% of the total surface area of obtained iron powder.

- For 30 h of milling, the particle size of obtained iron powder calculated by BET was approximately 100 nm; the particle size by FESEM observation was in the range of 50–85 nm; average micropore diameter was 18 nm; the crystal size reached 7 nm; the saturation magnetization was 145 emu g\(^{-1}\); the coercivity was 61.57 Oe. However, the nanoparticles can be clustered up to tens of micrometers as observed by the FESEM images. It is possible to make up the artifact in the analysis.

In addition, experimental results show that acetone did not cause spurious mill products, and ensured its role as an environmental protection for iron milling process. It can be applied to the fabrication of other materials susceptible to oxidation by high-energy ball milling technique.

The manufactured iron powder has been applied and used as an air oxygen reducer which possesses a very good ability to reduce the microclimatic oxygen concentrations in a hermetic mini-environment. The kinetic of oxygen reduction process of the iron powders will be presented in detail in another publication.

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