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Novel mechanochemical process for synthesis of magnetite nanoparticles using coprecipitation method

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ABSTRACT

A novel coprecipitation method using a high mechanical energy field as the synthesis reaction system of magnetite (Fe_3O_4) has been developed for preparing the superparamagnetic Fe_3O_4 nanoparticles with high crystallinity in water system. In the synthesis process, the suspension containing the precipitates of ferrous hydroxide and goethite was treated in a tumbling ball mill under a cooling condition. The mechanical energy generated by collision of ball media promoted the Fe_3O_4 formation reaction and simultaneously crystallized the formed Fe_3O_4 nanoparticles without using any conventional heating techniques by means of the mechanochemical effect. The collision energy of ball media was numerically analyzed by discrete element simulation of their motion in the ball mill. Size, crystallinity and magnetization of the Fe_3O_4 nanoparticles obtained under different ball-milling conditions were almost the same regardless of the amount of the collision energy. However, the reaction rate of Fe_3O_4 formation increased with the collision energy, which was analogous to increase of the reaction rate caused by increase of the heat energy applied to the reaction system. The reaction rate depended strongly on the number of collisions with the energy larger than a threshold value corresponding to the activation energy in this reaction system.

1. Introduction

Magnetite (Fe_3O_4) is one of the most important industrial materials because of the excellent magnetic properties, and Fe_3O_4 nanoparticles have been used formerly for various applications such as recording materials, pigments, etc. Recently, bio-applications of Fe_3O_4 nanoparticles have been studied actively: e.g., sensors [1–3], magnetic resonance imaging [4,5], drug delivery system [6,7] and cancer therapy [8–10]. In industrial production of Fe_3O_4 nanoparticles, synthesis methods using liquid phase reactions are often employed, in which Fe_3O_4 nanoparticles with uniform phase are obtained relatively easily: e.g., thermal decomposition [11], micro-emulsion [12], coprecipitation [13] and hydrothermal treatment [14]. Particularly, coprecipitation method in water system [15] has attracted much attention as a simple synthesis method with low environmental impact because the synthesis is carried out in aqueous solutions without using any organic solvents under mild reaction conditions of relatively low temperature. However, this advantage tends to lead to a significant disadvantage; the crystallinity and magnetic properties of Fe_3O_4 nanoparticles prepared without heating become relatively poor [16–18]. In order to improve the disadvantage, an annealing treatment is carried out after drying of the nanoparticles but simultaneously the nanoparticles agglomerate each other due to heat energy, leading to growth of the nanoparticles [17]. Addition of surfactant into the aqueous solution can prevent from agglomerating, resulting in inhibition of the particle growth [19,20]. For bio-applications, however, the nanoparticles should be washed fully to remove the surfactant; this complicates the synthesis process and spoils its advantage. Consequently, it is difficult to prepare simply ultrafine Fe_3O_4 nanoparticles with high crystallinity and excellent magnetic properties using conventional coprecipitation methods.

In order to overcome the disadvantage, we have developed a novel coprecipitation method using a high mechanical energy field as the synthesis reaction system. In this method, a cooled tumbling ball mill is used as the reaction field for inhibiting the particle growth caused by heat energy [21]. In addition, any additives such as oxidizing and reducing agents and surfactants are not required. Both the formation reaction and the crystallization can be progressed by using the mechanical energy (i.e., the mechanochemical effect) generated by collision of ball media instead of heat energy.

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Nomenclature

a	coefficient in Eq. (20) (s^{b-1})
b	coefficient in Eq. (20) (–)
E	collision energy of ball media per unit time (J s^{-1})
E_r	collision energy of ball media per single revolution of vessel (J)
$\boldsymbol{F}$	contact force acting on ball medium (N)
$\boldsymbol{F}_c$	centrifugal force acting on ball medium (N)
f	average number of contact points per unit time (s^{-1})
$\boldsymbol{g}$	gravity acceleration (m s^{-2})
I	peak intensity at $2\theta = 21.2°$ of sample obtained after ball-milling treatment (–)
I_b	inertia moment of ball medium (kg m^2)
I_m	peak intensity at $2\theta = 21.2°$ of sample obtained before ball-milling treatment (–)
k	coefficient (s^{-1})
k'	coefficient (–)
m	mass of ball medium (kg)
N	rotational speed of vessel (s^{-1})
$\boldsymbol{n}$	unit vector in normal direction at contacting point (m)
n_t	number of collisions with energy exceeding threshold value (s^{-1})
r	radius of ball medium (m)
$\boldsymbol{T}$	torque caused by tangential contact force (N m)
t	milling time (s)
$\boldsymbol{v}$	relative velocity of contacting balls (m s^{-1})
$\boldsymbol{X}$	position of ball medium (m)
x	amount of magnetite in product (mol)
Y	Young's modulus (Pa)

Greek letters

α	constant depending on restitution coefficient (–)
γ	content of magnetite in virtual product (%)
$\boldsymbol{\delta}$	overlap displacement between contacting balls (m)
η	damping coefficient (kg s^{-1})
κ_n	stiffness in normal direction (N $m^{-3/2}$)
κ_t	stiffness in tangential direction (N m^{-1})
μ	sliding friction coefficient (–)
ξ	diffraction intensity ratio defined by Eq. (18) (–)
σ	Poisson's ratio (–)
$\boldsymbol{\omega}$	angular velocity of ball medium (s^{-1})

Subscripts

b	ball
n	normal component
t	tangential component
w	wall

In this paper, the mechanical energy was numerically analyzed by simulating the behavior of ball media in the milling vessel by means of the discrete element method (DEM). Based on the analysis results, contribution of the mechanical energy to progress of the formation reaction was investigated, and the reaction mechanism in this system is discussed.

2. Experimental

All chemicals used in the experiments were of analytical reagent grade and were used without further purification. The concentration of ferrous and ferric ions in the starting solution was the same as that in the synthesis experiment which Wan et al. [22] performed. 1.5 mmol of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) and 3.0 mmol of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) were dissolved in 60 ml of deionized and deoxygenated water in a beaker. Thirty milliliter of 1.0 kmol/m^3 NaOH solution was added into the solution at a constant addition rate under vigorous stirring using a magnetic stirrer in an argon atmosphere, and then the dark brown suspension containing ferrous hydroxide ($Fe(OH)_2$) and goethite (α-FeOOH) was obtained. The pH value was higher than 12. The addition rate of NaOH solution was set to be 3.0 ml/min for forming the precipitates homogeneously. During preparation of the starting suspension, the suspension temperature was kept below 5 °C in order to inhibit progress of the reaction between $Fe(OH)_2$ and α-FeOOH, forming Fe_3O_4. The starting suspension thus prepared was poured into the milling vessel with an inner diameter of 90 mm and a capacity of 500 ml, made of stainless steel. Stainless steel balls with a diameter of 3.2 mm were used as the milling media, and the charged volume of ball media containing the void formed among them was 40% of the vessel capacity, as shown in Fig. 1. After replacement of air with argon in the milling vessel, the milling vessel was sealed. In order to promote the solid phase reaction between $Fe(OH)_2$ and α-FeOOH, the ball-milling treatment was then carried out by rotating the milling vessel at the rotational speed of 35–140 rpm (corresponding to 17–69% of the critical rotational speed (=202 rpm) determined experimentally based on the behavior of ball media containing the starting suspension) for a given time. During the ball-milling treatment, the milling vessel was cooled from its outside in a water bath. Temperature of the water bath was kept at 1.0 ± 0.1 °C, and inside temperature of the milling vessel was 1.6–1.7 °C regardless of the rotational speed; this means that the milling vessel was cooled thoroughly. After the ball-milling treatment, the precipitate was washed with deionized water and decanted after centrifugation at the centrifugal acceleration of 1500 G. The washing operation was repeated thrice and then the sample was dried under vacuum at 30 °C for 5 h. In order to investigate the mechanochemical effect on the formation reaction, the synthesis experiments without ball-milling were also carried out as follows: the starting suspension was sealed in a stainless steel bottle with a capacity of 200 ml, and then it was placed in the water bath kept at 1.6 °C for 12 h under static condition. The sample thus obtained was compared with those from the milling treatments.

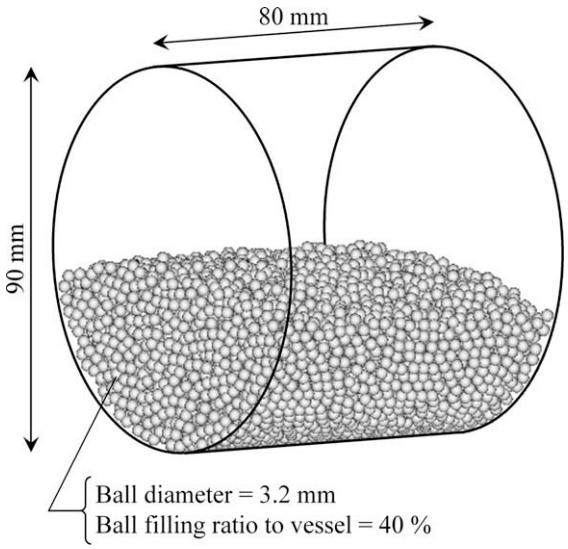

Fig. 1. Schematic of tumbling ball mill used in this work.