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Letter

Novel mechanochemical synthesis of fine $FeTiO_3$ nanoparticles by a high-speed ball-milling process

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ABSTRACT

Herein a novel mechanochemical approach to synthesize fine ilmenite $FeTiO_3$ nanoparticles using high-speed ball-milling with steel balls and TiO_2 nanoparticles is reported. The pure $FeTiO_3$ nanoparticles with a typical particle size of 15 nm were synthesized via a reaction between the TiO_2 nanoparticles, oxygen gas, and Fe atoms around the surface of the steel balls under local high temperatures induced by the collision energy in the ball-milling process.

Ilmenite $FeTiO_3$ is an interesting wideband gap (2.54 eV) antiferromagnetic semiconductor due to potential applications in numerous advanced devices such as optoelectronic, electromagnetic, and spintronic devices [1–6]. Recently, ilmenite $FeTiO_3$ has also been applied as a chemical catalyst and photocatalyst [7,8]. From the viewpoint of several key applications, fine $FeTiO_3$ nanoparticles have been eagerly anticipated.

The $FeTiO_3$ phase can be synthesized by a solid-state reaction at high temperature above 1200 °C under a vacuum [9–11]. However, this synthesis leads to large size particles and limited chemical homogeneity. In contrast, a liquid-phase reaction may realize fine and homogeneous $FeTiO_3$ nanoparticles, but this reaction is more troublesome than the solid-state reaction because the liquid-phase process requires delicate techniques [8] and/or the development of a sintering process to obtain a pure $FeTiO_3$ phase [12,13]. Hence, a liquid-phase process as a synthetic route for $FeTiO_3$ nanoparticles less than several ten nanometers has yet to be reported. On the other hand, a mechanochemical method may realize $FeTiO_3$ nanoparticles less than several ten nanometers since the mechanochemical route has several advantages compared to solid-state and liquid-phase reactions, including a simple, green process and the ability to obtain fine particles [14–16].

Generally, the mechanochemical method is characterized by the repeated welding, deformation, and fracture of the constituent powder materials [17]. Chemical reactions occur at the interfaces of the particles, which are continuously regenerated during milling [18]. Consequently, solid-state reactions can be promoted in a milling apparatus without external heating. Herein we report the first synthesis to realize fine $FeTiO_3$ nanoparticles with a typical particle size of 15 nm using a novel mechanochemical approach. $FeTiO_3$ nanoparticles are formed by the reaction between TiO_2 nanoparticles, oxygen gas, and Fe atoms around the surface of the steel balls by employing high-speed ball-milling.

The raw material was commercially available TiO_2 (ST-01, Ishihara Sangyo, Japan) with a mean particle size of 7 nm, which was calculated from the specific surface area (SSA). TiO_2 nanoparticles with a volume of 10 cm^3 were loaded into a 180 cm^3 cylindrical vial along with 50 cm^3 milling balls. The milling balls were commercial stainless steel balls such as SUS440C, which is a solid solution of iron (Fe, 83 wt.%), chromium (Cr, 16 wt.%), and carbon (C, 1 wt.%) with a 3 mm diameter. Mechanochemical treatment was performed by a high-speed ball-milling apparatus (High-G, Kurimoto Ltd., Japan) that operated for 3 h in an air atmosphere under various centrifugal forces. The phase evolution of the milled nanoparticles was characterized by X-ray diffraction (XRD; JDX-3530M, JEOL, Japan) using Ni filtered Cu-Kα radiation. The nanoparticles' morphologies were observed by transmission electron microscopy (TEM, JEM-2100F, JEOL, Japan).

Fig. 1 shows the XRD patterns of the raw TiO_2 nanoparticles and the milled nanoparticles under various centrifugal force conditions: 50, 100, and 150 gravity (G). As shown in Fig. 1(a), only peaks corresponding to an anatase-type crystal structure were observed for the TiO_2 nanoparticles before milling. After milling with a centrifugal force of 50 G, the TiO_2 crystal structure changed into the rutile-type

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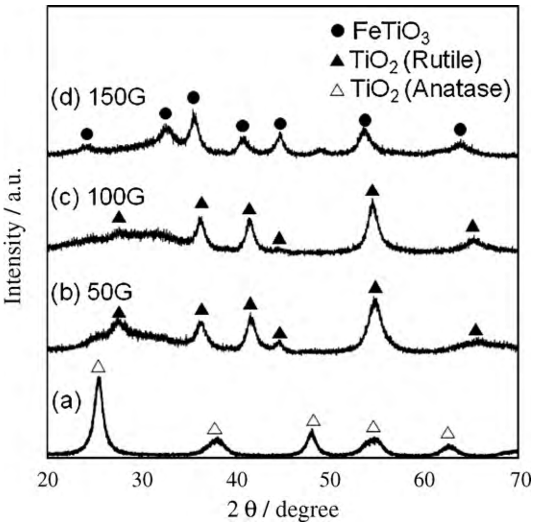

Fig. 1. Phase evolution of nanoparticles (a) before and (b)–(d) after ball-milling at various centrifugal forces.

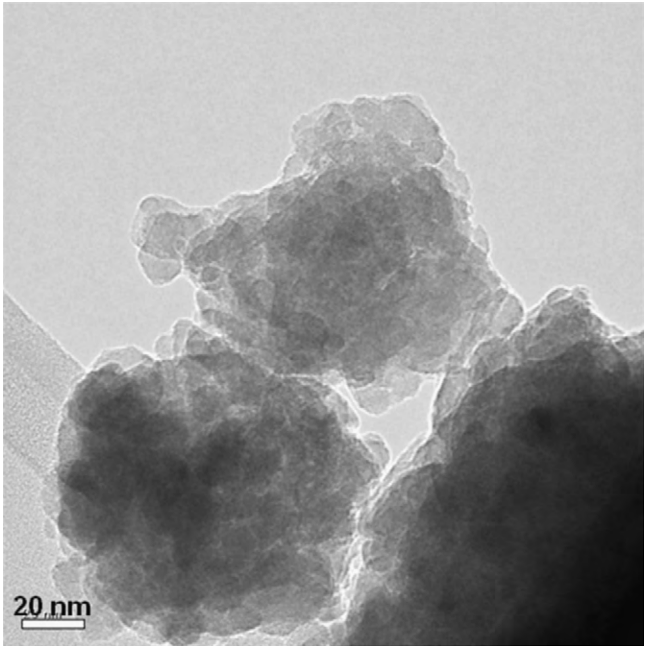

Fig. 2. TEM image of the synthesized $FeTiO_3$ nanoparticles.

(Fig. 1(b)). This change in the TiO_2 crystal structure by ball-milling agrees well with the previous report [19]. Similarly, ball-milling at 100 G resulted in the rutile-type TiO_2 (Fig. 1(c)). In contrast, ball-milling at 150 G drastically altered the peak patterns (Fig. 1(d)); diffraction peaks corresponding to a rhombohedral $FeTiO_3$ structure (JCPDS No. 75-1211) were observed without other impurity peaks and an average crystallite size of 12 nm was calculated using the Scherrer equation.

Fig. 2 shows the TEM image of the $FeTiO_3$ nanoparticles synthesized by high-speed ball-milling at a centrifugal force of 150 G. Although the $FeTiO_3$ nanoparticles aggregated, most of them were found to be about 15 nm in size. This finding is consistent with that calculated from XRD peaks. Some groups have reported the synthesis of $FeTiO_3$ nanoparticles by liquid-phase reactions [8,12,13], but all these nanoparticles had a particle size of about 100 nm. In contrast, the $FeTiO_3$ nanoparticles obtained in this study are very small compared those synthesized by liquid-phase reactions. Hence, we successfully synthesized fine $FeTiO_3$ particles for the first time. Fine $FeTiO_3$ nanoparticles synthesized by ball-milling may offer significant advantages for several key applications.

Fig. 3 schematically depicts the formation of $FeTiO_3$ nanoparticles via high-speed ball-milling of stainless steel balls and TiO_2 nanoparticles. Recently, we have found that the temperature in local regions around the surface of the steel balls probably increases up to several thousand degrees Celsius by the collision with 150 G [20]. Considering this finding and our results, the $FeTiO_3$ nanoparticles are likely formed by the high temperature reaction between TiO_2 nanoparticles, oxygen gas in the air, and Fe atoms around the surface of the steel balls by employing high-speed ball-milling.

The ball-milling process is common in grinding machines as well as in reactors where various functional materials can be created by mechanochemical synthesis. A simple milling process reduces both CO_2 generation and energy consumption during materials production. In a conventional mechanochemical synthesis, a solid-state reaction occurs at the interfaces of raw materials under high pressure conditions by mechanical action. In our ball-milling process, the chemical reaction occurs at the interface of the raw TiO_2 nanoparticles, oxygen gas, and Fe atoms around the surface of the steel balls under local high temperatures induced by the collision energy, which results in the formation of a pure $FeTiO_3$ phase. Therefore, this milling approach should realize an advanced method for mechanochemical synthesis of Fe based complex oxides.

In summary, fine $FeTiO_3$ nanoparticles were synthesized by a novel mechanochemical method using high-speed ball-milling of steel balls and TiO_2 nanoparticles. Most of the synthesized pure $FeTiO_3$ had a particle size of 15 nm. The $FeTiO_3$ nanoparticles were formed by the reaction between TiO_2 nanoparticles, oxygen gas, and Fe atoms around the surface of the steel balls under local high temperatures induced by the collision energy in the ball-milling process. We believe this mechanochemical process using high-speed, ball-milling of steel balls will realize the synthesis of various Fe based complex nanoparticles, including $FeTiO_3$, $LnFeO_3$ (Ln = La, Pr, Sm, Gd, Dy, and Yb), $CuFe_2O_4$, $NiFe_2O_4$, and $LiFePO_4$.

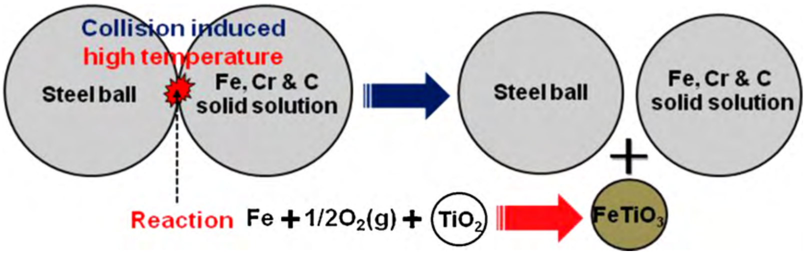

Fig. 3. Plausible scheme for the formation of $FeTiO_3$ by a novel ball-milling process.

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References

[1] Y. Ishikawa, S. Akimoto, J. Phys. Soc. Jpn. 13 (1958) 1110.
[2] D.S. Ginley, M.A. Butler, J. Appl. Phys. 48 (1977) 2019.
[3] P.F. McDonald, A. Parasiris, R.K. Pandey, B.L. Gries, W.P. Kirk, J. Appl. Phys. 69 (1991) 1104.
[4] P. Padmini, M. Pulikkathara, R. Wilkins, R.K. Pandey, Appl. Phys. Lett. 82 (2003) 586.
[5] N.C. Wilson, J. Muscat, D. Mkhonto, P.E. Ngoepe, N.M. Harrison, Phys. Rev. B 71 (2005) 75202.
[6] Y. Takada, M. Nakanishi, T. Fujii, J. Takada, Appl. Phys. Lett. 92 (2008) 252102.
[7] F. Liu, H. He, C. Zhang, Chem. Commun. (2008) 2043.
[8] Y.J. Kim, B. Gao, S.Y. Han, M.H. Jung, A.K. Chakraborty, T. Ko, C. Lee, W.I. Lee, J. Phys. Chem. C 113 (2009) 19179.
[9] C.H. Shomate, J. Am. Chem. Soc. 68 (1946) 964.
[10] B.F. Naylor, O.A. Cook, J. Am. Chem. Soc. 68 (1946) 1003.
[11] R.W. Grant, R.M. Housley, S. Geller, Phys. Rev. B 5 (1972) 1700.
[12] X. Tang, K.-a. Hu, J. Mater. Sci. 41 (2006) 8025.
[13] J. Mona, S.N. Kale, A.B. Gaikwad, A.V. Murugan, V. Ravi, Mater. Lett. 60 (2006) 1425.
[14] B.D. Stojanovic, J. Mater. Process. Technol. 143 (2003) 78.
[15] S. Ohara, H. Abe, K. Sato, A. Kondo, M. Naito, J. Eur. Ceram. Soc. 28 (2008) 1815.
[16] S. Ohara, A. Kondo, H. Shimoda, K. Sato, H. Abe, M. Naito, Mater. Lett. 62 (2008) 2957.
[17] T. Tsuzuki, P.G. McCormick, J. Mater. Sci. 39 (2004) 5143.
[18] C.C. Koch, in: R.W. Cahn (Ed.), Materials Science and Technology—A Comprehensive Treatment, vol. 15, VCH Verlagsgesellschaft GmbH, Weinhein, 1991, p. 193.
[19] K. Ishihara, T. Yokoi, K. Hara, Bull. Ceram. Soc. Jpn. 44 (2009) 813.
[20] S. Ohara, Z. Tan, J. Noma, T. Hanaichi, K. Sato, H. Abe, Solid State Commun. 150 (2010) 198.