2012

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Recommended Citation
Hao WU, Qiang LI. Application of mechanochemical synthesis of advanced materials. Journal of Advanced Ceramics 2012, 1(2): 130-137.

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Application of mechanochemical synthesis of advanced materials

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Received September 18, 2011; Accepted March 4, 2012
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Abstract: An overview is given of recent development of mechanochemical processes for the preparation of advanced ceramics. Some fundamental mechanical effects are firstly compared and discussed. Several important application fields are listed as follow, stemming from oxide materials, non-oxide materials, and composite materials to nano-structured materials.

Key words: mechanochemical; advanced materials; composite materials; nano scale

1 Introduction

Mechanochemical reaction is a process that a strong mechanical force proceeds materials destruction and causes a formation of a different structure. Mechanochemical method has been widely used in synthesis of advanced materials, covered almost all aspects of material science [1-3]. Mechanochemical process is a simple, environmental, low-cost technology. Interests in this field tend to rise continuously, and the number of related papers increases annually [4-6]. Even though the mechanisms of mechanochemical process are not completely clear.

In this review, we give some discussion of the mechanical effects during grinding, especially a new proposal of the mechanical effects of extrusion. Some important preparation works of advanced materials via mechanochemical process are summarized to demonstrate their application capability in the future.

Planetary ball mill is a typical machine in current use of mechanochemical process. The planetary ball mill performs grinding by continually revolving the large plate and rotating the containers concurrently. Both the plate revolution (centrifugal) speed and container rotation (planetary) speed are independently adjustable (Fig. 1). During grinding process, collision of balls plays an important role of energy transferring from balls to raw materials. After accepting mechanical energy from balls, the particles of raw materials rupture. So the particle size decreases, and specific surface and surface energy increase. These mechanical effects caused by collision can initiate significant structural changes and even chemical reactions in materials, which was defined as

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Fig. 1 A schematic diagram of the planetary ball mill
mechanochemical reactions [7,8].

1 Mechanisms of mechanochemical processes

Mechanochemical reaction may be employed in synthesis of materials, and replace the solid state reaction at high temperature. However, there are two drawbacks of planetary ball mill. Firstly, most of direct collision of balls or between balls and chamber are useless to act the raw material and cause the loss of energy. Secondly, the collision at exact moment just induces short-lived activation of raw materials, and probability of chemical reaction is very low. So the low efficiency of planetary ball mill results in time-consuming (several days), energy-consuming and low productivity.

In order to extend the acting time of mechanical effects, a new mechanical effect should be selected. Some new grinding machines were designed to change the mechanical effects [9,10]. The new mechanical effect of these new machines is shearing force instead of collision. We also develop a new machine called screw grinding machine (Fig. 2). When the screw in the center rotates, powders of raw materials are compressed by the screw again the chamber wall, and extrusion is acted on particles. So most of mechanical energy are transferred to raw materials. Compared to collision, extrusion can act on particles and activate raw materials for a long time. So mechanochemical reaction driven by extrusion can be much more efficient and time-saving (several hours). In addition, the products can be easily collected from grinding machine.

2 Synthesis of oxide materials

Early and major research works of mechanochemical synthesis are conducted at oxide materials. Stojanovic ever reviewed the research works of the formation of perovskite structure of BT, PT, PZT, PZN, PMN and LM ceramic materials by mechanochemical synthesis [11]. Zhang et al. synthesized a series of ABO$_4$-type oxide, and studied the relation between mechanochemical reactivity and the crystal structure in detail [12]. We also published some papers that reported the synthesis of complex oxide materials. Figure 3 is a typical SEM image of lead magnesiumniobate prepared by mechanochemical reaction. We found that high grind power can reduce the synthesis time, improve the purity of products and decrease the particle size [13] (Fig. 4).

![Fig. 3 SEM image of PMN prepared by mechanochemical reaction](image)

![Fig. 4 Effect of grinding power on phase composition of product](image)
We also successfully obtained Super Fine LiMn$_2$O$_4$ by a rapid mechanochemical process at low temperature [14] (Fig. 5).

From above research work, it was confirmed that mechanochemical process can be widely used in the synthesis of many important oxide ceramics.

3 Synthesis of non-oxide materials

When mechanochemical reaction is conducted at air atmosphere, oxide materials are usually synthesized. If the mechanochemical device can be gas tight and filled with inert gas, non-oxide materials can be prepared. Some non-oxide materials, such as ZrB$_2$, WC, AlN, etc. are successfully obtained via mechanochemical reactions at argon or nitrogen atmosphere [15-18].

ZrB$_2$ were produced by by magnesiothermic reduction, reaction (1), via mechanochemical process at argon atmosphere [16].

$$\text{ZrO}_2 + \text{B}_2\text{O}_3 + 5\text{Mg} = \text{ZrB}_2 + 5\text{MgO} \quad (1)$$

After 30 h of uninterrupted milling, ZrB$_2$ were formed. Figure 6 confirmed the existence of MgO and ZrB$_2$ at the end of 30 h uninterrupted milling treatment. The peaks of as-received ZrB$_2$ were intense and narrow. It is obviously that ZrB$_2$ has fine crystal structure. Another experiment of sample containing 30% excess Mg and B$_2$O$_3$ were preceded for 40 h milling. Fine phase of ZrB$_2$ were also obtained besides impurity of Fe due to long time milling. However, increasing both milling time and excess amounts of Mg and B$_2$O$_3$, unreacted ZrO$_2$ still remained. An additional treatment of 1M HCl was induced to remove MgO and Fe. As can be seen from Fig. 6, MgO and Fe can be completely removed.

Typical SEM image of product of mechanochemical process was shown in Fig. 7. Porous agglomerates of ZrB$_2$ and MgO was displayed, and ultrafine particles about 0.5 μm were found.

Vanadium nitride (VN) can be produced by mechanochemical process at a pressurized N$_2$ atmosphere [17], which is also a reactant. AlN was form by a solid-gas reaction, reaction (2).

$$2\text{V} + \text{N}_2 = 2\text{VN} \quad (2)$$

The analysis of XRD patterns (Fig. 8) display a broadening of Vanadium peaks due to comminution and refinement of Vanadium particles from 0.5 to 1.5 h at the same time the peaks of VN appear. After 4 h of milling, VN are the main phase shown in XRD patterns, in which the peaks of Vanadium disappear. Up to 8 h, the intensities of VN peaks continually rise.

The dimension of Vanadium metal and Vanadium
nitride cubic unit cell determined by XRD were enlarged while milling time was increased. The dimension of unit cell is sensitive to the nitridation level, which is obviously raised by prolonged milling time.

Morphology images (Fig. 9) of as-obtained VN ground under nitrogen atmosphere for 8 h by SEM exhibits agglomerated grains with size of 1-5 μm, and they are formed by nano-scale spherical particles.

4 Synthesis of composite materials

During mechanochemical process, homogenous dispersion and mixture of different components are its important functions. So mechanochemical process is very suitable for preparation of composite materials, and produces homogenous hybrid structure. Some synthesis of important composite materials was explored via mechanochemical process, for examples, some metal-oxide system [19-22].

Al2O3 is an important reinforcement candidate in the intermetallic compounds (IMC). Alumina reinforced intermetallic is provided with several advantages of high strength, good wear resistance and improved fracture toughness. So it is a good attempt to fabricate Al2O3/IMC composite by mechanochemical process. The new high temperature structural materials, Ti5Si3-Al2O3, were prepared by mechano-chemical reaction from raw materials of TiO2-Al-Si [23]. The mechanochemical reaction includes several steps:

\[
3\text{TiO}_2 + 4\text{Al} \rightarrow 2\text{Al}_2\text{O}_3 + 3\text{Ti} \quad (3) \\
3\text{Ti} + 1.8\text{Si} \rightarrow 0.6\text{Ti}_5\text{Si}_3 \quad (4)
\]

The XRD patterns (Fig. 10) of mixtures after different milling time confirm the formation of Ti5Si3. After the mixture was milled for 45h, the peaks of TiO2-Al-Si starting materials disappeared and only peaks of Ti5Si3 could be found. In suit formed Al2O3 have very fine size with an amorphous structure, and cannot be found in XRD pattern. But in suit formed Al2O3 with fine size prompt a homogenous reinforced structure and enhance the properties of composites.

Figure 11 displays the typical SEM photos of composites at different milling times. After long time of milling, the mixture was uniform and homogenous. Finally after 45 h of milling, agglomerated structure
consisted of nano-scale particles were formed. It can be known that nano-scale hybrid can improve the properties of composite materials.

Other serial composite materials are oxide materials. Mechanochemical process can also be utilized in the preparation of these composite materials [24-26].

A mixed cathode materials of LiMn$_2$O$_4$/LiCoO$_2$ was designed as a novel core-shell structure by mechanical activation (MA) [24].

Figure 12 presents SEM images of spinel before and after coating. The coating process by mechanical activation (MA) causes the decreasing of particle size of LiMn$_2$O$_4$, and compare favorably with the traditional solution precipitation method (Fig. 12b). The as-received composite grains are round-shaped, uniform in size, and loose agglomerates. Reduction of particle size and surface electrolyte interface of core-shell enhance the electrochemical performance of composite materials.
5 Synthesis of nano-structured materials

The most attractive feature of mechanochemical method is that it is an easy synthesis process of nano-structure materials. This conclusion can be necessarily reached from above research works. From those SEM images, nano-scale particles are always observed. So mechanochemical process are often applied to produce nano-structured materials [27-30].

Hydroxyapatite (HAp) is important bio-materials. A novel mechanochemical approach was created to synthesize nanorods and nanogranules of HAp [31]. In this work, two reactions were employed.

\[
6\text{CaHPO}_4 + 4\text{Ca(OH)}_2 \rightarrow \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 + 6\text{H}_2\text{O} \quad (5)
\]

\[
4\text{CaCO}_3 + 6\text{CaHPO}_4 \rightarrow \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 + 4\text{H}_2\text{O} + 4\text{CO}_2 \quad (6)
\]

XRD patterns of Fig. 13a reveal the formation of HAp in reaction (5). The XRD patterns confirmed that the product is HAp as expected besides impurity of CaHPO_4.

\[
6\text{CaHPO}_4 + 4\text{Ca(OH)}_2 \rightarrow \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 + 6\text{H}_2\text{O} \quad (5)
\]

\[
4\text{CaCO}_3 + 6\text{CaHPO}_4 \rightarrow \text{Ca}_{10} (\text{PO}_4)_6 (\text{OH})_2 + 4\text{H}_2\text{O} + 4\text{CO}_2 \quad (6)
\]

XRD patterns of Fig. 13a reveal the formation of HAp in reaction (5). The XRD patterns confirmed that the product is HAp as expected besides impurity of CaHPO_4.

In Fig. 13b after 40, 60 and 80 h of milling, the extra peaks of impurity are not observed and the only detected phase is HAp.

The different reaction routes of HAp preparation result in distinct morphology of products. Fig. 14 shows nanorods HAp from reaction (5) and nanospheres HAp from reaction (6).

A new attempt of utility of mechanochemical process in preparation of nano-structured materials is to synthesize nanosheets by mechanical cleavage process [32], which presents a novel approach to obtain the nanosheets starting from the layered compound.

Figure 15 exhibited the lighter and translucent nanosheets. The sizes of these nanosheets were in a range from 50 to 200 nm, which could be observed from the TEM image. The same mass-thickness contrast of nanosheets in TEM image meant that they had the uniform thickness.

6 Summary

Present research works have made great achievement

![XRD patterns of samples milled for 40, 60 and 80 h, reaction (5) (a) and reaction (6) (b). CaHPO_4 (■) and HAp(●)](image)

![Typical TEM micrograph of nanorods HAp for reaction (5) (a) and nanospheres HAp for reaction (6) (b) after 80 h milling time](image)
in many aspects of material synthesis. However the most exciting fields are the preparation of nano-structure materials and nanocomposites. Mechanochemical process supplies a novel route to design nano-structure, which is also environment friendly, low-cost, controllable and efficient.

Acknowledgement

The project is supported by National Natural Science Foundation of China (No. 20671035) and the Open Fund of Key Laboratory of High Performance Ceramics and Superfine Microstructures, Shanghai Institute of Ceramics, Chinese Academy of Sciences.

References

[1] Gajovic A, Santic A, Djerdj I, et al. Structure and electrical conductivity of porous zirconium titanate ceramics produced by mechanochemical treatment and sintering. J Alloys Compd 2009, 479: 525-531.
[2] Ni X, Ma J, Li JG, et al. Microwave characteristics of Co/TiO2 nanocomposites prepared by mechanochemical synthesis. J Alloys Compd 2009, 46: 386-391.
[3] Xu X, Tang JY, Nishimura T, et al. Synthesis of Ca-a-SiAlON phosphors by a mechanochemical activation route. Acta Mater 2011, 59: 1570-1576.
[4] Tojo T, Zhang QW, Saito F. Mechanochemical synthesis of FeSbO4-based materials from FeOOH and Sb2O3 powders. Powder Technol 2008, 181: 281-284.
[5] Hea Q, Wang HZ, Wen GH, et al. Formation and properties of BaxFe2-yO3 with spinel structure by mechanochemical reaction of Fe2O3 and BaCO3. J Alloys Compd 2009, 486: 246-249.
[6] Rojac T, Trtnik Ž, Kosec M. Mechanochemical reactions in Na2CO3-M2O5 (M=V, Nb, Ta) powder mixtures: Influence of transition-metal oxide on reaction rate. Solid State Ion 2011, 190: 1-7.
[7] Zoltán Juhász A. Aspects of mechanochemical activation in terms of comminution theory. Colloids Surf A- Physicochem Eng Asp 1998, 141: 449-462.
[8] Venkatalaman KS, Narayanan KS. Energetics of collision between grinding media in ball mills and mechanochemical effects. Powder Technol 1998, 96: 190-201.
[9] Iwasaki T, Satoh M, Koga T. Analysis of collision energy of bead media in a high-speed elliptical-rotor-type powder mixer using the discrete element method. Powder Technol 2001, 121(2-3): 239-248.
[10] Ohara S, Abe H, Sato K. Effect of water content in powder mixture on mechanochemical reaction of LaMnO3 fine powder. J Eur Ceram Soc 2008, 28: 1815-1819.
[11] Stojanovic DB. Mechanochemical synthesis of ceramic powders with perovskite structure. J Mater Process Technol 2003, 143-144: 78-81.
[12] Zhang QW, Tojo T, Tongamp W. Correlation between mechanochemical reactivity forming ABO4-type complex oxides and the structures of product materials. Powder Technol 2009, 195: 40-43.
[13] Wu H, Chen C, Jiang DY, et al. Fast mechanochemical synthesis of nano-structured PMN at low temperature. J Inorg Mater 2010, 25(5): 541-545.
[14] Song J, Xu B, Huang DX, et al. Synthesis, structure and properties of super fine LiMn2O4. Adv Mater Res 2011, 177: 9-11.
[15] Kameshima Y, Irie M, Yasumori A, et al. Mechanochemical effect on low temperature synthesis of AlN by direct nitridation method. Solid State Ion 2004, 172: 185-190.
[16] Akgün B, Erdem Çamurlu H, Topkaya Y, et al. Mechanochemical and volume combustion synthesis of ZrB2. Int J Refract Met Hard Mater 2011, 29(5): 601-607.
[17] Roldan MA, López-Flores V, Alcala MD, et al. Mechanochemical synthesis of vanadium nitride. J Eur Ceram Soc 2010, 30: 2099-2107.

Fig. 15  Transmission electron microscopic image of Ti5NbO14 nanosheet
[18] Sakaki M, Bafghi MS, Vahdati Khaki J, et al. Effect of the aluminum content on the behavior of mechanochemical reactions in the WO$_3$-C-Al system. *J Alloys Compd* 2009, 480: 824-829.

[19] Mohammad Sharifi E, Karimzadeh F, Enayati MH. A study on mechanochemical behavior of B$_2$O$_3$-Al system to produce alumina-based nanocomposite. *J Alloys Compd* 2009, 482(1-2): 110-113.

[20] Sabooni S, Mousavi T, Karimzadeh F. Mechanochemical assisted synthesis of Cu(Mo)/Al$_2$O$_3$ nanocomposite. *J Alloys Compd* 2010, 497: 95-99.

[21] Mohammad Sharifi E, Karimzadeh F, Enayati MH. Synthesis of titanium diboride reinforced alumina matrix nanocomposite by mechanochemical reaction of Al-TiO$_2$-B$_2$O$_3$. *J Alloys Compd* 2010, 502: 508-512.

[22] Mohammad Sharifi E, Karimzadeh F, Enayati MH. Preparation of Al$_2$O$_3$-TiB$_2$ nanocomposite powder by mechanochemical reaction between Al, B$_2$O$_3$ and Ti. *Adv Powder Technol* 2011, 22: 526-531.

[23] Sabooni S, Karimzadeh F, Abbasi MH. A study on the mechanochemical behavior of TiO$_2$-Al-Si system to produce Ti$_5$Si$_3$-Al$_2$O$_3$ nanocomposite. *Adv Powder Technol* 2012, 23(2): 199-204.

[24] Kosova NV, Devyatkina ET, Kaichev VV, et al. From ‘core-shell’ to mixed cathode materials for rechargeable lithium batteries by mechanochemical process. *Solid State Ion* 2011, 192(1): 284-288.

[25] Mahajan S, Prakash C, Thakur OP. Piezoelectric properties of 0.5(PbNi$_{1/3}$Nb$_{2/3}$)O$_3$-0.5Pb(Zr$_{0.32}$Ti$_{0.68}$)O$_3$ ceramics prepared by solid state reaction and mechanochemical activation-assisted method. *J Alloys Compd* 2009, 471: 507-510.

[26] Ebrahimi-Kahrizsangi R, Nasiri-Tabrizi B, Chami A. Synthesis and characterization of fluorapatite titania (FApeTiO$_2$) nanocomposite via mechanochemical process. *Solid State Sci* 2010, 12: 1645-1651.

[27] Dodd CA. A comparison of mechanochemical methods for the synthesis of nanoparticulate nickel oxide. *Powder Technol* 2009, 196: 30-35.

[28] Baláz P, Dutková E, Skorvánek I, et al. Kinetics of mechanochemical synthesis of Me/FeS (Me=Cu, Pb, Sb) nanoparticles. *J Alloys Compd* 2009, 483: 484-487.

[29] Plashnitsa VV, Gupta V, Miura N. Mechanochemical approach for fabrication of a nano-structured NiO-sensing electrode used in a zirconia-based NO$_2$ sensor. *Electrochim Acta* 2010, 55: 6941-6945.

[30] Mancheva M, Iordanova R, Dimitriev Y. Mechanochemical synthesis of nanocrystalline ZnWO$_4$ at room temperature. *J Alloys Compd* 2011, 509: 15-20.

[31] Nasiri-Tabrizi B, Honarmandi P, Ebrahimi-Kahrizsangi R, et al. Synthesis of nanosize single-crystal hydroxyapatite via mechanochemical method. *Mater Lett* 2009, 63: 543-546.

[32] Zhang N, Chu J, Li CX, et al. A facile route to synthesize the Ti$_5$NbO$_{14}$ nanosheets by mechanical cleavage process. *J Am Ceram Soc* 2010, 93(2): 536-540.