Investigation of the magnetic properties and fracture behavior of Nd–Fe–B alloy powders during high-energy ball milling

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Abstract

In this work, Nd–Fe–B alloy powders are fabricated via high energy ball milling and their fracture behavior and magnetic properties are investigated at different milling times. The powder characteristics (particle shape, size, size distribution, and microstructure) and magnetic properties of the Nd–Fe–B alloys are systematically analyzed. The initial spherical Nd–Fe–B powder is cracked/crushed even after a short period of milling (30 s) due to the high impact energy generated during high energy ball milling. These randomly cracked polygonal-shaped powders are fragmented after 5 min of milling and converted to fine powders. Interestingly, the fine particles after milling for 5 min are conducive to agglomeration at longer milling times (20–60 min) and formed spherically-shaped agglomerated powder. Additionally, the sphericity of the powder increased to 92% by re-pulverization and agglomeration at 60 min. The milled powder shows the Nd3Fe14B phase, and the x-ray diffraction patterns exhibit peak broadening with increasing milling time, clearly confirming the powder refinement behavior by high energy ball milling. The magnetic properties of the milled powders are systematically investigated and their behavior is elucidated as a function of the milling time.

1. Introduction

Nd–Fe–B magnets have long retained the top position, as the most powerful magnets known to industry [1, 2]. Commercially, Nd–Fe–B alloy powders are manufactured by strip casting, melt-spinning, HD (Hydrogen Decapitation), and jet-milling processes [3]. Another useful and powerful cutting-edge powder metallurgical process is gas atomization (GA) [4]. Gas atomization can directly produce Nd–Fe–B alloy powder from the melted Nd–Fe–B alloy without any treatment process. With conventional processes such as strip casting and melt spinning, the microstructure can only be controlled through the solidification parameters [3, 5]. However, controlling the powder morphology and surface is very hard, compared to the Nd–Fe–B powders produced by gas atomization. Moreover, it is hard to obtain uniform properties in the bulk when the bulk or molded bulk is prepared from such powders.

The high energy ball milling process is one of the alternative methods for overcoming the above-mentioned difficulties. The method provides many advantages, including controlling the surface, shape, and size of the powders, and the formation of amorphous and nano-grained microstructure [5–7]. Even though some reports are available in the literature on the general microstructural aspects of mechanically alloyed powders [8–12], there are no reports yet on controlling the microstructure, shape, and size of powders by high energy ball milling.
Also, no studies have reported how using powders with different shapes and sizes obtained by high energy ball milling affects the control of formability.

In this study, the shape, size, surface, and grain sizes of the Nd–Fe–B powders were controlled using high energy ball milling. Results showed the formability and density of the Nd–Fe–B alloy powders were increased by employing this nanostructuring approach. The effect of milling time on the powder morphology and magnetic properties of Nd–Fe–B powders were systematically investigated. Additionally, the formability and density of Nd–Fe–B powders were investigated, as a function of the shape, surface, size, and grain size of the Nd–Fe–B powder.

2. Materials and methods

2.1. Sample preparation
Nd–Fe–B isotropic powders obtained from MQP-S (Nd–Pr–Fe–Co–Ti–Zr–B, Magnequench) are used in the present investigation. The Nd–Fe–B powders are milled using a high energy ball milling machine (PLANETARY MILL P100, TAEMYONG SCIENTIFIC Co., Ltd), and zirconia as milling media (milling jars and balls). The ball to powder weight ratio (BPR) is kept at 10:1 with a milling speed of 800 RPM. The milling time is fixed at the 30 s, 5 min, 20 min, and 60 min. The as-received Nd–Fe–B powders are stored in a glove box purged with Ar gas to prevent powder contamination.

2.2. Analysis of fracture behavior
The powder characteristics such as powder morphology, crystal structure, particle size distribution, and cross-section microstructure of the Nd–Fe–B powder have been examined. The morphology and cross-sectional microstructure of both unmilled and milled Nd–Fe–B powders are observed by scanning electron microscopy (SEM, MIRA LMH-II, TESCAN) and transmission electron microscopy (TEM, JEM-2100F, JEOL). The crystal structure of the Nd–Fe–B powders is analyzed using x-ray diffraction (XRD) (MiniFlex-600, Rigaku). The particle size distribution and the sphericity of the powders are measured using a particle size analyzer (RT-1800, Bettersize). The magnetic properties of both the un-milled and milled Nd–Fe–B powders are measured by the vibrating-sample magnetometer (VSM, VersaLab VSM, Quantum Design Inc.).

3. Results and discussion

3.1. Fracture behavior of Nd–Fe–B powder at different milling times
In this section, the effect of milling time on the powder shape, particle size and size distribution, and its sphericity are systematically investigated. Figure 1 shows the morphology of the initial unmilled Nd–Fe–B powder, and the powders milled for the 30 s, 5 min, 20 min, and 60 min by the high-energy milling process. The particles of the initial Nd–Fe–B powder (figure 1(a)) have a smooth surface and a spherical shape without any pores or defects on the surface. Figure 1(b) shows the morphology of the powder milled for the 30 s, showing that the spherical powders have started to be broken down even after a short milling duration. It is evident that most of the initial spherical powder is fractured and forms different morphologies, such as angular and irregular shapes. Interestingly, the spherical powders were crushed even after the 30 s of milling due to the large energy impact forces applied during high energy ball milling (figure 1(b)). The high magnification micrograph in figure 1(b) reveals that powder fracture was initiated by the compressive stress applied with high impact energy to the powder from the left side and right side during ball milling. As a result, many micro-cracks are formed randomly in different directions, which are clearly indicated by the yellow arrows on the powder surface. This kind of brittle fracture behavior of Nd–Fe–B alloy is expected since it contains an intermetallic phase. However, spherical powders over 20 μm size are still present after the 30 s of milling. As the milling time was increased, the morphology of the powder totally changed. It was observed that the resulting powder particles became less than 20 μm in size (figure 1(c)), mainly due to fractures induced by the ball-powder collisions, and partially from the powder-powder collisions during high energy ball milling for 5 min. The powders became more angular and irregular in shape and some of the powders were noted to be in an agglomerated state. When the milling time was increased from 5 to 20 min (figure 1(d)), the powders were completely crushed, and changed into rounded, angular, irregular, and agglomerated forms. Also, some of the formed submicron powder became attached to the coarse powder, as shown in the high magnification micrograph (inset in figure 1(d)). However, the powder size increased when milling time increased from 5 to 20 min. This behavior is mainly dependent on the cold-welding taking place between the small and irregular powders during milling, which resulted in an agglomeration state. After 60 min, the Nd–Fe–B powder shape had dramatically changed, and particle size decreased to below 10 μm compared to the initial powders and the powders milled for other times. Interestingly, some of the powders were found to be rounded, and some had angular shapes.
To examine the powder fracture mechanism that occurs during high energy ball milling, the cross-sectional microstructure of Nd–Fe–B powders were analyzed for different milling times, as shown in figure 2. The initial gas-atomized powder in figure 2(a) shows a neat microstructure without any defects or pores on the surface of the powder. It is clearly seen that cracks are generated inside the spherical powder by external forces/stress during the high energy ball milling, even after the 30 s (figure 2(b)). As milling time increased, the shape of the powder changed to an angular shape due to the continuous external stress, as seen in figure 2(c). The pulverized powder became agglomerated when milling time increased to 20 min (figures 2(d) and (e)). Interestingly, after 60 min the large-sized agglomerated powder changed to a fine agglomerated powder under 10 μm, as shown in figure 2(f). In addition, many tiny and fine nano-structured particles were clearly observed.

Figure 3 shows the particle size distribution of the Nd–Fe–B powders prepared by high energy ball milling for different milling times. It is evident that the initial particle size has a wide size distribution of about 10 ~ 100 μm, which is consistent with the powder morphology shown in figure 1(a). The particle size distribution of the Nd–Fe–B milled powder showed a broad size distribution with increasing milling time. The powder size
sharply decreased, even after the 30 s, then gradually showed a bimodal size distribution for 5- and 20 min of milling time. However, the bimodal distribution slowly vanished with increasing milling time, and an almost Gaussian peak was noted after 60 min of milling.

In addition, the average particle size and sphericity of the Nd–Fe–B powders were analyzed to understand the characteristic behavior of the milled powders in more detail. The results are presented in figure 4. It is obvious that the average particle size is around 40 μm for the initial powder, and rapidly decreased when the powders were milled for the 30 s to 5 min. Thereafter, the average particle size of the powder gradually decreased, to 9 μm at 60 min. The sphericity of the initial (unmilled) powder was measured to be 99.9% since the initial powder is produced by gas atomization. At the milling intervals of the 30 s, and 5 min, the sphericity of the powder gradually vanished due to repeated collisions between the powder and balls, and powder and jars (see figure 1). However, the sphericity (about 92%) abruptly increased when milling time increased to 20 min, due to the occlusion of the fine powder by the coarse powder. In addition, the tips on the surface of the angular shaped powder were exposed to more friction during longer high energy ball milling times and turned spheroidal. This mechanism is explained later in detail (under section 3.5).

3.2. TEM analysis of Nd–Fe–B powder

To further understand the powder behavior during high energy ball milling, TEM analysis was conducted for the initial unmilled and 60 min-milled powder. Figures 5(a) and (c) show the low magnification TEM images of the

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Figure 3. The powder size distribution of Nd–Fe–B powder fabricated by high energy ball milling with various milling time, initial state, 0.5, 5, 20, and 60 min, respectively.

Figure 4. Mean particle size and sphericity of the gas atomized Nd–Fe–B powder and milled powders with different milling times.
initial and 60 min milled Nd–Fe–B powders, respectively. Figures 5(b) and (d) show their corresponding high magnification TEM images. It is clearly observed that the initial powder has a multi-scale grain structure which contains both fine as well as coarse grains. The black contrast region in the high magnification image (figure 5(b)) represents the Nd$_2$Fe$_{14}$B phase, and the white stripes the Nd-rich phase, which have formed a few nanometers in range. On the other hand, in the powder milled for 60 min (figure 5(c)), the grains are very fine and refined as the grain size is below 20 nm and much finer than the initial powder. Interestingly, after milling for 60 min the microstructure transformed into an amorphous phase, which can be clearly identified in the high magnification TEM image shown in figure 5(d).

TEM-EDS analysis was next carried out to follow the phase evolution and chemical composition with milling time. The area mapping, and dot mapping composition analyses of the Nd–Fe–B powders are presented in figure 6 and table 1, respectively. It can be clearly identified from the HAADF STEM results that the white contrast area is Zr-rich with low Nd content; the dark grey area is Nd$_2$Fe$_{14}$B phase with the correct stoichiometric composition. All the other minor elements in MQP-S (magnequench), such as Pr, Co, Ti, and Zr, were also identified in the EDS spectra.

Further quantitative analysis of the different elements is presented in table 1. It is observed that the grain and grain boundaries of the initial powder are composed of Nd$_2$Fe$_{14}$B and Nd-rich phase, respectively. However, the powder milled for 60 min showed a remarkable increase in the Zr-rich phase compared with the initial powder.

### 3.3. Crystal structure of Nd–Fe–B powder

Investigation of the crystal structure of the Nd–Fe–B milled powder was carried out using X-diffraction analysis, and the results are shown in figure 7. All the peaks are well indexed to the Nd$_2$Fe$_{14}$B phase (JCPDS # 00-036-1296), and the initial powder of the Nd$_2$Fe$_{14}$B phase is clearly crystalline. However, the width of the major Nd$_2$Fe$_{14}$B peak started increasing from the 30 s, and the powder is fully amorphized after 60 min. The Nd$_2$Fe$_{14}$B

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**Figure 5.** (a) Low magnification TEM image of the Nd–Fe–B initial state powder, (b) High magnification TEM image of the Nd–Fe–B initial state powder showing Nd$_2$Fe$_{14}$B matrix with randomly oriented grains, (c) Low magnification TEM image of the Nd–Fe–B milled powder with 60 min milling, (d) High magnification TEM image of the Nd–Fe–B milled powder with 60 min milling showing nano polycrystalline Nd$_2$Fe$_{14}$B matrix.
phase did not change to any other phase even though the peak intensity decreased with amorphization, in addition to peak broadening. This result is well consistent with the TEM results (shown in figure 5).

3.4. Magnetic properties of the Nd–Fe–B milled powder
The magnetic properties such as coercivity and magnetization of the Nd–Fe–B milled powder are determined by the physical property measurement system (PPMS), shown in figure 8. In the whole hysteresis loop in figure 8(a),
The saturation magnetization is gradually decreased with increasing milling time. The enlargement region of magnetization and coercivity is presented in Figure 8(b). It is evident from Figure 8(b) that the magnetization of the initial powder is about 73.48 emu g\(^{-1}\). However, the value of magnetization is slightly increased up to 76.61 emu g\(^{-1}\) after the 30 s (0.5 min), then decreased gradually with increasing milling time. The 60 min powder exhibit the lowest magnetization value of about 54.78 emu g\(^{-1}\). The overall decrement of the magnetization is mainly due to the grain refinement during the high energy ball milling. On the other hand, the coercivity of \(-2.8\) kOe is obtained for initial powders, and its value is increased up to \(-7.7\) kOe after 30 s milling time. However, the coercivity is slightly decreased further increasing milling time. The grain refinement as well as the formation of Zr-rich phases is mainly responsible for the decrement of magnetic properties (magnetization, and coercivity) with increasing milling time. It is evident from Figure 6 that the Zr-rich phase is identified with low Nd content, and showed a remarkable increase in the Zr-rich phase with milling time compared with the initial powder. During high energy ball milling, the Zr element in the master alloy (MQP-S) could not react with other elements, since it is hard to pulverize, even when ZrO\(_2\) milling media is used. This could promote the precipitation of high content Zr from the Nd-rich and Nd\(_4\)Fe\(_{14}\)B matrix phases in the grain boundary during high energy ball milling. Recently, Capehart et al\([13]\) reported Zr addition on Nd–Fe–B alloys and argued that the Nd\(_{2.6}\)Fe\(_{14}\)BZ\(_{0.4}\) phase was formed by the substitution of Nd. Furthermore, Shaaban et al\([14]\) argued that the enrichment of Zr in the Nd-rich phase after the casting of NdFeB was the main reason for the formation of the Nd\(_4\)Fe\(_{17}\) phase. This phase is harmful to magnetic properties. As a result, magnetization is decreased by the Zr-rich phase. Meanwhile, coercivity is increased when the non-ferromagnetic phase is increased, which affects the magnetic screening.

### 3.5. Fracture mechanism of mechanically milled Nd–Fe–B powder

The overall mechanical behavior and fracture mechanism of the Nd–Fe–B powders are shown schematically in Figure 9. It is evident from the figure that the spherical Nd–Fe–B powder (step 1) gets cracked/crushed/fractured...
even after a short period of milling (step 2) due to the high impact energy generated during high energy ball milling. These randomly cracked powders with polygon shapes in step 3 have a dramatic effect on the fillability, fluidity, and compressibility of the powder during sintering or molding. As the milling time is continued, a fine powder is formed, and the growth of sphericity due to agglomeration between the fine powder and the milled powder begins, as can be observed in the 4th and 5th stages. These spherically shaped agglomerated powders can improve the filling property, fluidity, and compressibility better than the milled powder. Thus, the moldability and packing density of the powders is expected to increase with longer milling times.

4. Conclusions

Nd–Fe–B powder was successfully fabricated, and the powder characteristics, as well as magnetic properties, were studied as a function of milling time during high energy ball milling. The initial spherical powder was pulverized by applied compressive stress, which caused the deformation of the powder and cracks to be generated inside the powder during the milling process. At longer milling times (at 20–60 min), a fine powder is formed, and sphericity starts to increase, due to agglomeration between the fine powders. These spherical shaped agglomerated powders can enhance filling property, fluidity, and compressibility better than the initial powder, or powders milled for short times. Meanwhile, TEM analyses indicate the presence of nanostructured grains with the Nd$_2$Fe$_{14}$B phase, and the Nd-rich phase, which formed with a few nanometers in length. The magnetization behavior was observed to gradually decrease with increasing milling time. The HADDF-STEM and EDS results revealed that the formation of a Zr-rich phase with low Nd content can strongly diminish magnetization behavior at higher milling times.

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