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The effect of Li$_3$N addition by mechanical alloying on Nd$_2$Fe$_{14}$B—Formation of NdN$_2$

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The effect of Li3N addition by mechanical alloying on Nd2Fe14B—Formation of NdN2

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Curie temperatures of R2Fe17 and RTiFe11 (R=rare earths) can be raised drastically by addition of interstitial nitrogen. Can one see similar effects in Nd2Fe14B? This question is particularly interesting because Nd2Fe14B’s relatively low Curie temperature has limited its applications in high temperature operations. Nitrogen additions by heat treating Nd2Fe14B in flowing N2 at different temperatures have been reported to raise its Curie temperature by 20–50 °C. We report an attempt of nitriding Nd2Fe14B by mechanical alloying it with Li3N. Our attempt resulted in the formation of a rare form of neodymium nitride, NdN2. The original goal to nitride Nd2Fe14B by mechanical alloying it with Li3N seems to be inapplicable.

Nd2Fe14B, discovered in 1981 by Croat,1 possesses excellent permanent magnetic properties and is an ideal material to replace the most used Sm-Co magnets. However, a serious drawback of Nd2Fe14B is its low operating temperature, i.e., the coercivity decreases so rapidly with increasing temperature that the practical operating temperature is only about 100 °C.2 On the other hand, it was recently discovered that interstitial nitrogen addition to R2Fe17 (R=rare earths) could raise its Curie temperature Tc by approximately 400 °C.3 A drastic increase in Tc (~200 °C) was also observed in K11Fe11 upon absorption of nitrogen.4 An obvious question is then how such nitrogen addition will affect the Curie temperature of Nd2Fe14B. Nitrogen addition by heat treating Nd2Fe14B samples in flowing N2 at different temperatures could only raise its Tc by 20–50 °C,5–7 possibly due to the limited number of nitrogen atoms going into the Nd2Fe14B lattice. As a matter of fact, the interstitial sites available to nitrogen in Nd2Fe14B are smaller in size and less in number than those in R2Fe17 and RTiFe11.8 It is unclear yet if the nitrogen atoms occupy interstitial or substitutional sites in Nd2Fe14B.

We report an attempt to improve the solubility of nitrogen in Nd2Fe14B, that is to nitride nanocrystalline Nd2Fe14B by mechanical alloying it with Li3N. This approach is based upon the following observations and arguments. First, mechanical alloying offers one of the few methods for mixing two ordinarily immiscible materials.9 This is probably due to the intimate contact between two components and subsequent intermixing of one component into another brought by the high energy ball-sample-container collisions during mechanical alloying. We expect that mechanical alloying will increase the solubility of nitrogen in Nd2Fe14B. Second, Li3N will be used as the source to provide nitrogen in a condensed state. Because of the relatively weak bonding in Li3N, a possible solid state displacement reaction, i.e., reduction of Li3N to pure Li and formation of Nd2Fe14B nitride, is anticipated. In fact, mechanical alloying induced displacement reactions have been reported in several publications.10–12 Third, it is well known that mechanical alloying produces nanocrystalline particles.13 Such extremely fine particles will enhance the possibility that nitrogen atoms go into the bulk of sample during mechanical alloying. It will also maximize the reaction rate by providing a larger surface area.

The Nd2Fe14B sample was prepared from elements by melting the constituents in an arc furnace under argon partial pressure. The amount of iron used was 9% less than the ideal 2:14:1 ratio, i.e., the actual atomic ratio Nd:Fe:B was 2:12:7:1. This was to minimize the amount of α-Fe that would be present in the product. During arc melting sample was turned over and remelted several times in order to reach homogeneity. After cooling down to room temperature, the sample was sealed in a quartz tube under helium atmosphere and heated to and maintained at 1100 °C for 2 h, and then quenched into a water bath. X-ray diffraction pattern of the powder sample was obtained using a SCINTAG diffractometer, and it showed the formation of the Nd2Fe14B phase [see Fig. 1(a)]. A small amount of bcc α-Fe was still present as indicated by the peak marked in Fig. 1(a).14

Prior to mechanical alloying, an attempt was made to heat directly the mixture of Nd2Fe14B and Li3N powders in a sealed quartz tube under helium atmosphere to see if the anticipated displacement reaction would occur. Such attempts resulted in explosions as soon as the temperature reached near 400–500 °C due to decomposition of Li3N. Therefore, a low temperature synthesizing process seemed to be necessary in order to overcome the problems associated with the decomposition of Li3N. Mechanical alloying could offer us a possible solution because it is a low temperature process. As a matter of fact, mechanical alloying is normally conducted at room temperature, and the maximum local temperature where the ball-sample-container collision takes place is less than 300 °C.9 As will be seen later, however, our study indicated that mechanical alloying probably led to the decomposition of Li3N as well.
Mechanical alloying was carried out as follows. Powders of Nd$_3$Fe$_{14}$B (obtained as described above) and Li$_3$N (purchased from Johnson Matthey) were mixed at a weight ratio of 8:1. This weight ratio corresponds to a molar ratio of about Nd$_3$Fe$_{14}$B:Li$_3$N = 1:4. The mixture was poured into a tungsten carbide (WC) vial in a glove-box and sealed in an argon atmosphere. Also sealed in the WC vial was a 11-mm-diam WC ball. The weight ratio of ball to sample was about 2:1. The powders were mechanically alloyed by milling with a Spex 8000 mixer/mill. A portion of the sample was taken out for x-ray examination after milling for 1 and 5 h, respectively, and the remaining were milled again until a total of 26 h had been reached. Because the mechanical alloyed samples were very reactive in the air, they were loaded on the diffractometer sample holder with N$_2$ flowing around them. During x-ray experiments sample chamber was kept under N$_2$ atmosphere.

Figures 1(b)–1(d) show the x-ray patterns of Nd$_3$Fe$_{14}$B-Li$_3$N samples after 1, 5, and 26 h of mechanical alloying, respectively. The sample after 1 h of mechanical alloying had a rather complex x-ray pattern [Fig. 1(b)]. Although peaks from Nd$_3$Fe$_{14}$B could still be identified, their intensities were reduced compared to that of the Nd$_3$Fe$_{14}$B sample before mechanical alloying. The appearance of some new phases is obvious as seen from the added peaks in its x-ray spectrum. These new phases are believed to be the combinations of NdN$_2$ (see below), Li$_3$N, α-Fe, and some unidentified intermediate phases.

Figure 1(c) is the x-ray pattern of the sample after 5 h of mechanical alloying. This sample had a relatively well-defined x-ray spectrum. As a matter of fact, all of the major peaks in the spectrum could be indexed as the ones from hexagonal NdN$_2$ and bcc α-Fe. The formation of NdN$_2$ and the substantial increase in the intensity of α-Fe peak indicated that Nd$_3$Fe$_{14}$B and Li$_3$N reacted in such a way during mechanical alloying that α-Fe precipitated out from the matrix and the excess neodymium formed NdN$_2$. NdN$_2$, which crystallizes in hexagonal La$_2$O$_3$-type structure with lattice parameters $a=3.79$ Å and $c=5.99$ Å, was first synthesized from Nd and N$_2$ under high pressure (30–300 atm) in an autoclave. We believe that the condition inside the WC vial during mechanical alloying was reminiscent of that in the autoclave. The high energy ball milling first led to the decomposition of Li$_3$N into Li and N$_2$, and then N$_2$ pressure gradually built up as a result of the continuation of such decomposition. At the same time, reaction between N$_2$ and Nd$_3$Fe$_{14}$B resulted in the precipitation of α-Fe and made the neodymium, probably in the form of NdN, available to further combine with pressured N$_2$ to form NdN$_2$.

Shown in Fig. 1(d) is the x-ray pattern of the sample after 26 h of mechanical alloying. Those peaks from NdN$_2$ and α-Fe were smeared out, and virtually no peak was present at all. This represents the situation where the sample, after 26 h of mechanical alloying, has been ground into extremely fine particles, perhaps in the nanometer range, as reported in other cases. This sample could consist of nanocrystalline particles of NdN$_2$, α-Fe, and some minor impurity phases. There was no evidence that any substantial amount of Nd$_3$Fe$_{14}$B was left in the sample. The magnetic measurement confirmed this conclusion. Nd$_3$Fe$_{14}$B was, however, present in the sample after 5 h of mechanical alloying as shown in Fig. 1(c).

Magnetization $M$ was measured as a function of temperature $T$ from room temperature to $\sim 600$ °C using a Faraday magnetometer. The magnetic field used was about 1 kG. Figure 2(a) shows the $M$ vs $T$ plot for the sample after 26 h of mechanical alloying. Because this sample is air sensitive, it was sealed in a small quartz tube during measurement. For comparison, the $M$ vs $T$ curve for a sample undergone no mechanical alloying (as quenched) is also shown [Fig. 2(b)]. The transition temperature of 310 °C for the as-quenched sample was consistent with the reported value of the Curie temperature of Nd$_3$Fe$_{14}$B. The
In summary, a rare form of neodymium nitride, NdN₂, was synthesized as the result of mechanical alloying Nd₂Fe₁₄B and Li₃N. The original goal to nitride Nd₂Fe₁₄B by mechanical alloying it with Li₃N seems to be inapplicable.

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