

## Enhancement of magnetic anisotropy of L1<sub>0</sub>-FeNi nanoparticles and the related compounds for realization of rare-earth free magnet

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In recent years, with the growing awareness of the environment, expectations for the development of high-performance motors for reducing power consumption are increasing. Especially in the automobile industry, the shift to electrified vehicles is progressing rapidly on a global scale, and the importance of high-performance motors is increasing year by year. General automobiles are equipped with more than 100 motors, including a drive main motor, and there is a demand for improved performance and cost reduction of motor products. The functions required of magnets vary depending on the intended use of the motor, such as high magnetization, high coercive force, heat resistance, and rust prevention. For products that are required high torque, such as drive main motors, strong magnets with high coercive force and high magnetization are required. In addition, heat resistance is also important because it is expected to be used under high load. On the other hand, water pumps, oil pumps, etc. are required to have rust prevention properties rather than magnetic performance. In future magnet development, not only the improvement of the maximum energy product ( $BH$ )<sub>max</sub> of the magnet but also the variety of functions will be important.

Meanwhile, the material we focused on was L1<sub>0</sub>-FeNi. L1<sub>0</sub>-FeNi is a material discovered in the 1960s, which is known to be present in iron meteorites in very small amounts.<sup>1)</sup> Although L1<sub>0</sub>-FeNi does not contain rare earths, its uniaxial magnetic anisotropy energy ( $K_u$ ) is  $1.3 \times 10^6$  J/m<sup>3</sup> and its saturation magnetization is 1.6 T, which is expected to be comparable to neodymium magnets. In addition, the Curie temperature of L1<sub>0</sub>FeNi is said to be 550 °C or higher, so it can be expected to be used at high temperatures. A lot of studies on L1<sub>0</sub>-FeNi have been made to date,<sup>1)-7)</sup> but most of them were fundamental; the degree of order and/or the fraction of L1<sub>0</sub>-phase were not enough.

Aiming at the practical application of L1<sub>0</sub>-FeNi, we have developed the Nitrogen Insertion and Topotactic Extraction method (NITE)<sup>8)</sup> as a method that can stably synthesize high-quality L1<sub>0</sub>-FeNi. A schematic diagram of the NITE method is shown in Fig. 1. The long-range order parameter ( $S$ ) of L1<sub>0</sub>-FeNi prepared by the NITE method was  $S = 0.71$ , and the coercive force was 142 kA / m. This coercive force is small for application as a magnet. The small coercive force seems to be caused by crystal grains are not magnetically isolated by sintering and  $K_u$  is low. In particular, improving  $K_u$  is important from the viewpoint of securing the potential of materials.

We are trying to improve  $K_u$  of L1<sub>0</sub>-FeNi by two approaches. The first approach is to improve the  $S$ . In general,  $K_u$  of L1<sub>0</sub>-type ordered alloy is said to increase in proportion to the square of  $S$ .<sup>5),9)</sup> In the NITE method, the ordered structure of L1<sub>0</sub>-FeNi inherits the structure of the precursor FeNiN. Therefore, in order to obtain L1<sub>0</sub>-FeNi with high  $S$ , it is important that Fe and Ni are completely ordered in the state of FeNiN. Therefore, in order to understand the ordered state of FeNiN, the arrangement of Fe, Ni, and N atoms was investigated using neutron diffraction. In conclusion, it was found that FeNiN is ordered by about 100% in Fe and Ni, and N atoms are in the Fe atomic plane. It was found that the denitriding process needs to be improved as the new issue to improve the  $S$  of L1<sub>0</sub>-FeNi. Another approach to improving  $K_u$  is to increase tetragonality. L1<sub>0</sub>-FeNi has a  $c / a$  value is almost unity showing contrast to other L1<sub>0</sub> type ordered alloys such

as FePt with 0.96 of  $c/a$ .<sup>10)</sup> Theoretical studies have been conducted to improve  $K_u$  if the crystals can be distorted to change  $c/a$ . In this study, we propose ordered-FeNi-N<sub>x</sub> ( $x = 0$  to 1) in which an arbitrary amount of nitrogen is introduced into L1<sub>0</sub>-FeNi as a means for changing  $c/a$ . According to the first principles calculations,  $K_u = 1.61 \times 10^6 \text{ J/m}^3$  was obtained for  $c/a = 1.025$  at  $x = 0.25$ , and  $K_u = 1.96 \times 10^6 \text{ J/m}^3$  for  $c/a = 0.992$  at  $x = 0.5$ , leading to larger  $K_u$  than that of L1<sub>0</sub>-FeNi. It is considered that  $K_u$  is improved by the tetragonality of the crystal structure by N-doping. The ordered-FeNi-N<sub>x</sub> was synthesized by topotactic nitriding of L1<sub>0</sub>-FeNi. As a result, the nitride had two phases with  $x$  of 0.5 and 1.0, and the nitrogen content was not continuously controlled. For  $x = 0.5$  the crystal structure as shown in Fig. 2 is expected. From the crystal structure analysis, the lattice constants were estimated to be  $a = 3.78 \text{ \AA}$ ,  $c = 3.73 \text{ \AA}$ , and  $c/a = 0.988$ , and we have succeeded in distorting the crystal by introducing N as theoretically expected. However, the magnetic measurement gave the coercive force of ordered-FeNi-N<sub>0.5</sub> much smaller than that of L1<sub>0</sub>-FeNi. The reason for the discrepancy with the calculation results is currently under investigation.

In order to put L1<sub>0</sub>-FeNi into practical use as a magnet, we need to work on further improving  $S$ , making crystals tetragonality, and magnetically isolating crystal grains.

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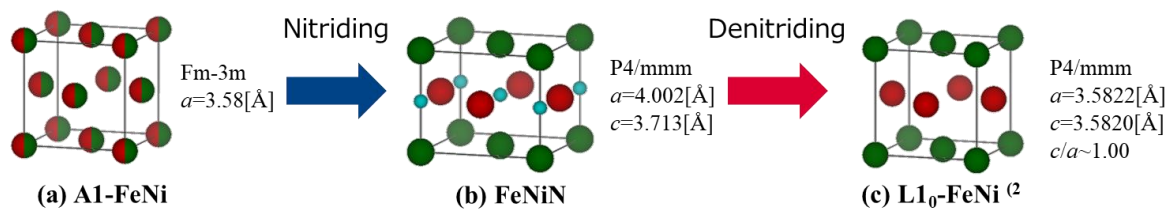


Fig.1 Conceptual diagram for fabrication path of ordered FeNi alloys by NITE method Models of crystal lattices for (a) A1-FeNi, (b) FeNiN, and (c) L1<sub>0</sub>-FeNi are depicted with Fe (red), Ni (green), and N (light blue) atoms. Atoms identified by red and green indicate that Fe and Ni are randomly arranged according to the ratios of colored areas.

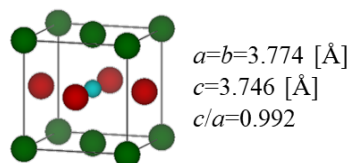


Fig.2 Crystal structure model of ordered-FeNi-N<sub>0.5</sub>. This structure is expected to have a smaller  $c/a$  value than L1<sub>0</sub>-FeNi.