

Combinatorial search of Fe-Ni-Cr system magnetostrictive alloys for force sensors

Takuya MAETANI*, Yutaka NAKAMITSU**, Junpei SAKURAI*,
Shigeki NAKAGAWA** and Seiichi HATA*

* Department of Mechanical Engineering, Nagoya University

Furo-cho, Chikusa-ku, Nagoya 464-8603, JAPAN

E-mail: hata@mech.nagoya-u.ac.jp

** Tokyo Institute of Technology

4259 Nagatsuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, JAPAN

Received 28 October 2014

Abstract

Magnetostrictive materials of the Fe-Ni-Cr ternary system for sensitivity enhancement of force sensors were searched by using a combinatorial method. Magnetostrictive materials for force sensors require large magnetostriction, high relative permeability, and high resistivity. This research is an attempt to find composition ranges that satisfy the following requirements: magnetostriction greater than 20×10^{-6} , relative permeability greater than 4,000, and resistivity over $90 \mu\Omega \text{ cm}$. A novel combinatorial deposition method, known as Combinatorial New Facing Targets Sputtering (Combi-NFTS) method was applied to fabricate libraries of samples with various compositions. Samples for measurement of the relative permeability and resistivity were synthesized with a composition distribution by using Combi-NFTS onto a $108 \text{ mm} \times 76 \text{ mm}$ glass substrate. After deposition of thin film, each sample is divided into $10 \text{ mm} \times 10 \text{ mm}$. The relative permeability and resistivity were measured by using a vibrating sample magnetometer and the four probe method, respectively. Bilayer cantilever samples for evaluation of magnetostriction were fabricated onto a $6 \text{ mm} \times 20 \text{ mm} \times 0.1 \text{ mm}$ Si substrate, whereby deflection of the samples changes when a magnetic field is applied. The laser lever method was used to measure the cantilever deflection. The results indicate that the composition range with an Fe content of 26-36.5 at.%, a Ni content of 61-66 at.%, and a Cr content of 7.5-9.5 at.% satisfy the requirement criteria.

Key words: Combinatorial method, Magnetostriction, Sensor, Magnetostrictive material, Permeability, Resistivity, Combinatorial sputtering

1. Introduction

The combinatorial method, (Xiang, et al., 1995) is a useful method that is used to search for new materials or optimize compositions, especially for alloy materials. With this method, samples that have different compositions or fabrication conditions are synthesized at one time. The characteristics of each sample are then evaluated in an efficient way (Hata, et al., 2006), (Yamauchi, et al., 2006). There are several sample fabrication methods, such as sputtering or laser molecular beam epitaxy. However, to fabricate samples with different compositions requires moving masks to limit the deposition area.

In our recent work, we proposed the Combinatorial New Facing Targets Sputtering, (Maetani, et al., 2012) (Combi-NFTS) method, which is a novel co-sputtering method. Composition graduated samples could be fabricated by using this sputtering method, but without the need for moving masks. Samples fabricated by Combi-NFTS have relatively linear composition graduation and the composition distribution range can be controlled by changing the distance between targets and the substrate. Furthermore, Combi-NFTS can confine the plasma and secondary electrons by the magnetic field created between the facing targets, so that thermal damage and physical damage due to collision of the plasma or secondary electrons to the deposited film are reduced, (Hoshi, et al., 1982).

Magnetostrictive materials have received attention for the conversion of electromagnetic energy into kinetic energy. Moreover, magnetostrictive materials exhibit features that include fast response to a change of magnetic field, high power, and noncontact control. Magnetostrictive materials are thus used for various sensors and actuators, such as displacement sensors, (Lemarqu and Lemarquand, 1992), (Seco, et al., 2004) torque sensors, (Wakiwaka and Mitamura, 2001), and high output pumps, (Bushko and Goldie, 1991).

Various magnetostrictive materials, (Sandlund, et al., 1994), (Mori, et al., 1983), (Clark, et al., 1972), (Elmen, 1983), such as rare-earth-iron compounds TbFe_2 , $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_{1.9}$ and FeNi alloys have been reported. As an example, rare-earth-iron compounds TbFe_2 , $\text{Tb}_{0.3}\text{Dy}_{0.7}\text{Fe}_{1.9}$ have large magnetostriction over 1000×10^{-6} and relative permeability less than 100. $\text{Fe}_{22}\text{Ni}_{78}$ has high relative permeability over 10,000 and magnetostriction less than 20×10^{-6} . Therefore, these materials do not both large magnetostriction and high relative permeability. The resistivities of reported magnetostrictive materials are generally less than $50 \mu\Omega \text{ cm}$.

In the case of the sensors that use these materials, there are problems in that a large magnetic field is required (rare-earth-iron compounds) due to low permeability or the sensitivity is not sufficient due to low magnetostriction (FeNi alloy). Thus, to solve these problems, new magnetostrictive materials are required that have both large magnetostriction and high relative permeability. The alternative magnetic field is often used for sensors. Thus, high resistivity is also required to prevent eddy-current loss.

In this paper, we search for magnetostrictive materials that have large magnetostriction, relative permeability and resistivity to improve the sensitivity of sensors in FeNiCr ternary systems. Firstly, resistivity and relative permeability were evaluated to limit the searching region to improve searching efficiency. Then, magnetostriction was evaluated. The desired value of magnetostriction is over 20×10^{-6} , relative permeability is over than 4,000 and resistivity is over than $90 \mu\Omega \text{ cm}$. Desired value of magnetostriction, permeability and resistivity are higher than $\text{Fe}_{22}\text{Ni}_{78}$, rare-earth-iron compounds, reported magnetostrictive materials, respectively.

2. Sample fabrication

Figure 1 shows a schematic of the Combi-NFTS method, which consist of a vacuum chamber and plasma box. The Fe and Ni targets are set-up facing each other, while the Cr target is set-up in the vertical position with respect to the other targets. In this sputtering method, target placed vertical position with substrate has composition distribution. Therefore a substrate attached at position 1 with a target-substrate distance (TS distance) of ca. 5 mm achieve a composition distribution of Fe, Ni and Cr, while when attached at position 2 with a TS distance of ca. 82 mm, the Cr composition is almost uniform.

A library to evaluate the resistivity and relative permeability was fabricated using $104 \text{ mm} \times 76 \text{ mm}$ borosilicate glass substrate in position 1 to achieve a composition distribution of all elements. The substrate was ultrasonically degreased in the successive rinses of acetone, ethanol, and pure water. The sputtering conditions employed are shown in Table 1. The sputtering time was adjusted to obtain a film thickness of ca. $1 \mu\text{m}$. After deposition of the thin films,

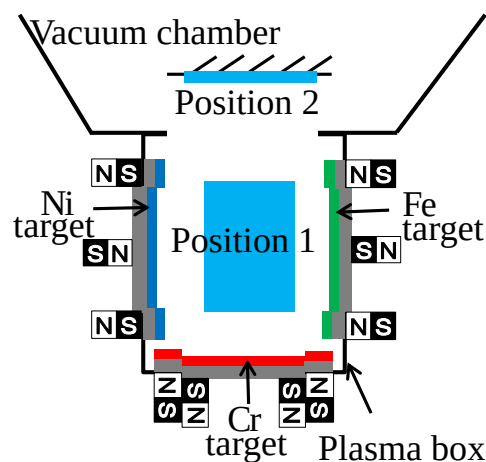


Figure 1. Schematic diagram of the setup for the Combi-NFTS method

the library was cut and divided into 10 mm×10 mm samples to evaluate resistivity and relative permeability. The composition of each as-sputtered sample was measured by using energy-dispersive X-ray spectroscopy (EDX; μ EDX-1300, Shimadzu). Five measurement points of each sample were used: 1 mm inside from the corner and at the center of the sample. The difference in the compositions of the five points was less than 2 at.% and the EDX resolution is ca. 1 at.%. This result indicates that the sample has a uniform composition. Figure 2 shows the compositions of the fabricated libraries using sputtering condition shown in Table. 1. The composition range of these libraries is enough wide to evaluate the resistivity and relative permeability.

Samples to evaluate magnetostriction were fabricated using a 6 mm×20 mm×0.1 mm Si substrate, which was ultrasonically degreased in the successive rinses of acetone, ethanol, and pure water, in position 2 to obtain almost uniform compositions. The sputtering time was adjusted to obtain a film thickness of ca. 300 nm. A FeNiCr/Ta/Cr trilayer was used to prevent detachment of the film from the substrate and to reduce increasing of initial deflection when the sample was annealed. The composition measurement of the FeNiCr for the trilayer sample by using EDX detect the under layer Cr ingredient together. Therefore, the composition of the FeNiCr was measured using a single layer sample fabricated with the same sputtering conditions.

Table 1. Sputtering conditions for library 1 to 8

	Library number	Ni	Fe	Cr
DC power [W]	1	600	300	150
	2	600	300	100
	3	600	300	80
	4	500	500	135
	5	1000	400	150
	6	900	400	150
	7	800	400	150
	8	900	400	100

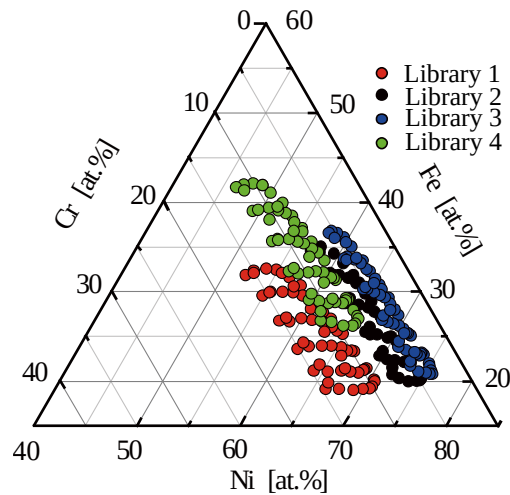


Figure 2. Compositions of library 1 to 4

3. Evaluation method

The resistivities of the as-sputtered samples were measured by using the four probe method (Roresta-GpMCP-T610, Mitsubishi Chemical Analytech Co.). The resistivity of the sample was defined as the average of four measurements. The measurement time to make 1 time measurement for each sample was less than 1 min.

Relative permeability was measured by using a vibrating sample magnetometer (VSM; Riken Denshi Co.) with in-plane magnetization measured. A magnetic field was applied in the in-plane direction of the thin film. The maximum

applied magnetic field was 2000 A/m, and the magnetic field was changed to produce a magnetization curve within 10 min. The measurement time for each sample was ca. 40 min.

It was considered that the resistivity and magnetic properties are changed by annealing; therefore, the influence of annealing was investigated. Yamamoto et al. reported, (Yamamoto, et al., 1960) the magnetic properties of a 5 at.%-Mo permalloy, which were improved by annealing at temperatures higher than the Curie temperature. In this paper, the samples were annealed by using vacuum furnace with an IR heating system (IVF298-2, Thermo Riko Co.) The annealing condition was used as follows. The base pressure was less than 1.0×10^{-3} Pa, the heating rate was 10 K/min from room temperature to 773 K, holding for 1 h, followed by natural cooling. 773 K is higher than the Curie temperature of $\text{Fe}_{15.6}\text{Ni}_{80.4}\text{Cr}_{4.0}$, (Rassmann and Hofmann, 1968). The sample was synthesized using a 52 mm $\times$ 76 mm borosilicate glass substrate in position 2 with the sputtering conditions given in Table 1. The compositions of fabricated libraries are shown in fig. 3 (a). After deposition of the thin films, samples were divided from the library for resistivity and magnetization measurements. The resistivity and magnetization curves for the as-sputtered samples are shown in fig. 3 (b), (c), respectively. After measurement, the samples were annealed. Figures 4 (a) and (b) show the measured resistivity and magnetization curves for the annealed samples. The as-sputtered samples had resistivities between 50 and 90 $\mu\Omega$ cm. The resistivity was decreased up to a maximum of 5 $\mu\Omega$ cm by the annealing process, which is ca. 10 %. However, the resistivity of the samples with Cr content greater than 4 at.% decreased less than 1 %. The trend for the change in the resistivity was the same before and after annealing. From this result, library 1 to 4 for the as-sputtered samples were used for evaluation of the resistivity to increase the material search efficiency. On the other hand, the magnetic properties of saturation magnetization and relative permeability were clearly improved by the annealing process. Therefore, library 1 to 4 for the annealed samples were used for evaluation of the relative permeability.

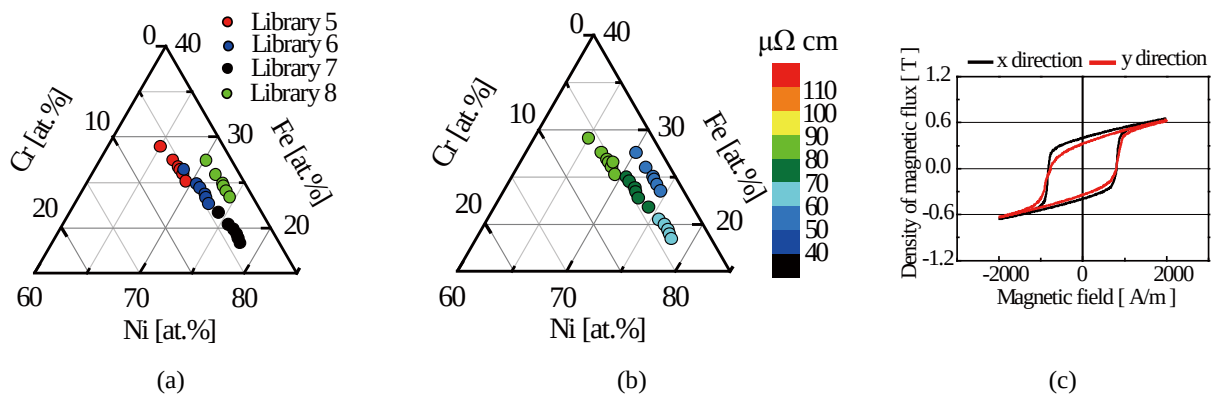


Figure 3. Measurement result for as-sputtered samples (a) Compositions of library 5 to 8, (b) Distribution of resistivity, (c) Magnetization curves

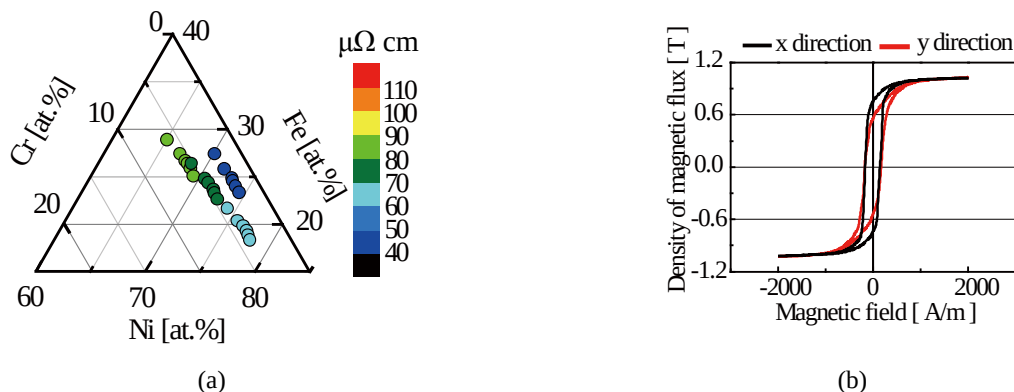


Figure 4. Measurement result for annealed samples (a) Distribution of resistivity, (b) Magnetization curves

Magnetostriction is characterized by using a laser lever method. Figure 5 shows a schematic diagram of the setup for the magnetostriction measurement. Two position sensitive detectors (PSD) are used to characterize magnetostriction; one as a reference and the other to measure deflection of the cantilever. The position of PSD 2 is adjusted as the differentials of the output voltage for PSD 1 and PSD 2 is zero in each measurement time. When a

magnetic field is applied, strain occurs only in the magnetostrictive material. A non-magnetic material is used as a substrate in which no strain occurs. Deflection of the bilayer cantilever thus occurs from the strain differential of the two layers. Magnetostriction of each sample is evaluated by the change in the distance at PSD 2 comparing to the reference material. The sample, which has composition of $\text{Fe}_{37.8}\text{Ni}_{62.3}$, is used as the reference material. $\text{Fe}_{37.8}\text{Ni}_{62.3}$ has magnetostriction, (Bozorth, 1953) of ca. 25×10^{-6} . Magnetic field was applied short side direction of the substrate. The magnetostriction of the sample was defined as the average of 10 measurements. The measurement time to make 10 measurement for each sample was ca. 40min.

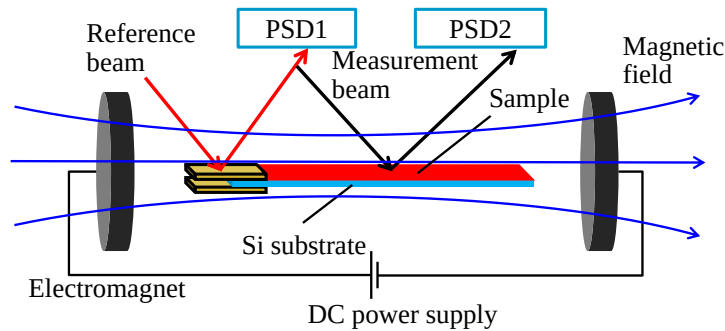


Figure 5. Schematic of the experimental setup for the magnetostriction measurements

4. Results and discussion

Figure 6 shows a color map for the resistivity of as-sputtered samples. The resistivity increases with the Cr content in the compositions. The resistivity is not clearly changed with the Fe and Ni contents in the compositions. The resistivity for bulk materials of Fe, Ni and Cr are 8.9, 6.2 and $12.7 \mu\Omega \text{ cm}$, respectively, where Cr has the highest resistivity of the three. Therefore, it is reasonable that the resistivity is dependent on the Cr content in the composition. The samples within the red line in fig. 6 have Cr contents greater than 7.5 at.% and satisfy the required resistivity of over $90 \mu\Omega \text{ cm}$. The resistivities of 240 samples were measured in the present work.

Figure 7 shows a color map for relative permeability of annealed samples. The relative permeability tended to increase with a decrease of the Cr content in the compositions, however there is not clearly trend with the Fe and Ni contents in the compositions. Cr is only non-magnetic material of the three materials comprising the thin films; therefore, it is reasonable that relative permeability is dependent on the Cr content. The samples within the blue line in fig. 7 have Cr contents less than 14 at.% and satisfy the required relative permeability of over than 4,000.

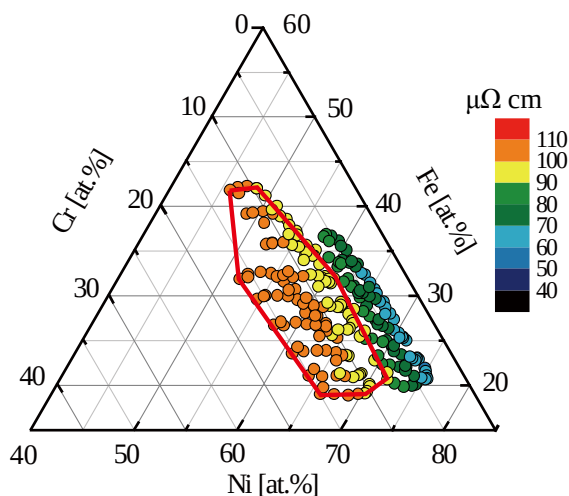


Figure 6. Distribution of resistivity for as-sputtered samples

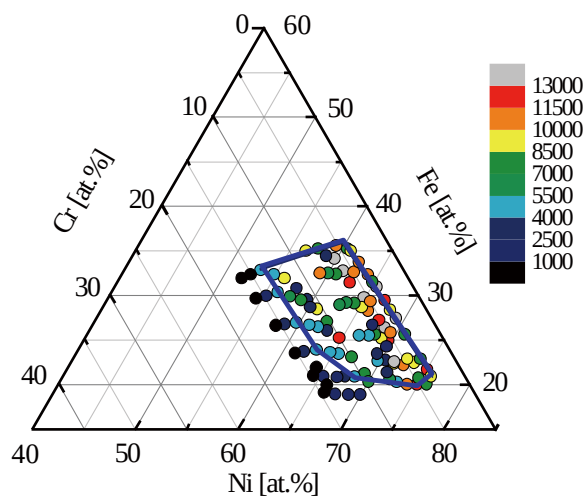


Figure 7. Distribution of relative permeability for annealed samples

Figure 8 shows the measurement result for the magnetostriction of reference material. The one division of the vertical axis of fig.8 expresses 1.5 μm . The displacement of the measurement beam on the PSD 2 for reference material is 10.4 μm . Comparing to the displacement of the reference material, samples which with displacement greater than 8 μm satisfy the required magnetostriction of 20×10^{-6} . Figure 9 shows a color map for the magnetostriction of annealed samples. The magnetostriction increases as the Cr content decreases and Fe content increases, however it is not clearly changed with the Ni content. Cr is the only non-magnetic material of the three, Fe has the positive magnetostriction; therefore, it is reasonable that magnetostriction is dependent on the Cr and Fe content in compositions. Ni has the negative magnetostriction, therefore it is expected that magnetostriction decrease with the Ni content increase. Furthermore, we expected there is a zero point of magnetostriction like what is observed in Fe-Ni system, (Bozorth, et al., 1953). The samples within the green line of fig. 9 have Cr contents from 3 to 9.5 at.% and Fe contents of 26 to 36.5 at.%, and satisfy the required magnetostriction of over 20×10^{-6} . These trends are in relative accord with the studies of Klokholm, (Klokholm and Aboaf, 1981), and Berger, (Berger, 1965). According to Berger, magnetostriction of Fe-Ni alloys is a function of the number of electrons/atom. Additional a little Cr to the Fe-Ni alloys, which decrease number of electron/atom, will have a positive influence on magnetostriction. For this study, additional Cr of almost samples is more than 5 at.%, nonmagnetic properties of Cr strongly appears to the relative permeability and magnetostriction.

From the resistivity, relative permeability and magnetostriction measurements, the compositions within the yellow area of fig. 10 satisfy all of the required values. The full sequence of evaluation for the magnetostrictive materials described in this paper (fabrication, compositional analysis, measurement of resistivity, relative permeability, and

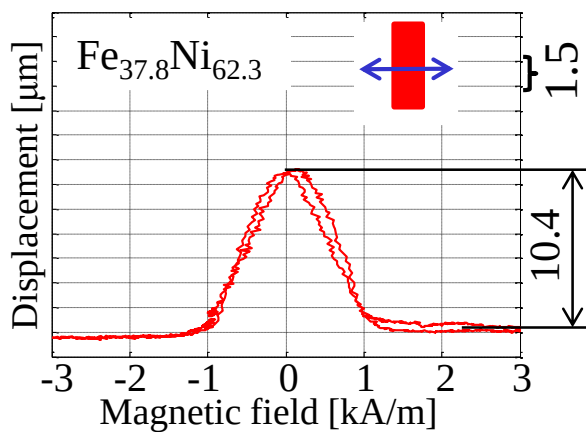


Figure 8. Magnetostriction measurement result for the ($\text{Fe}_{37.8}\text{Ni}_{62.3}$) reference material

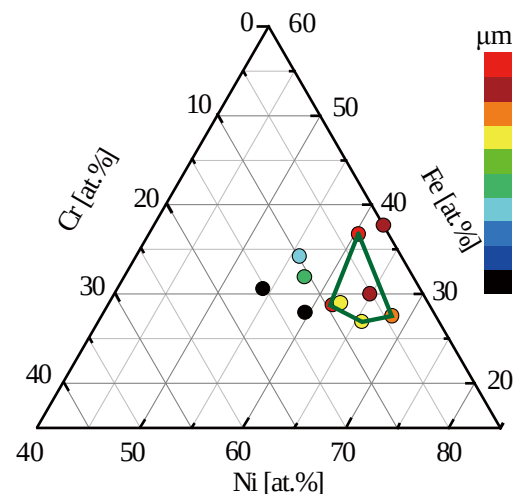


Figure 9. Distribution of magnetostriction for annealed samples

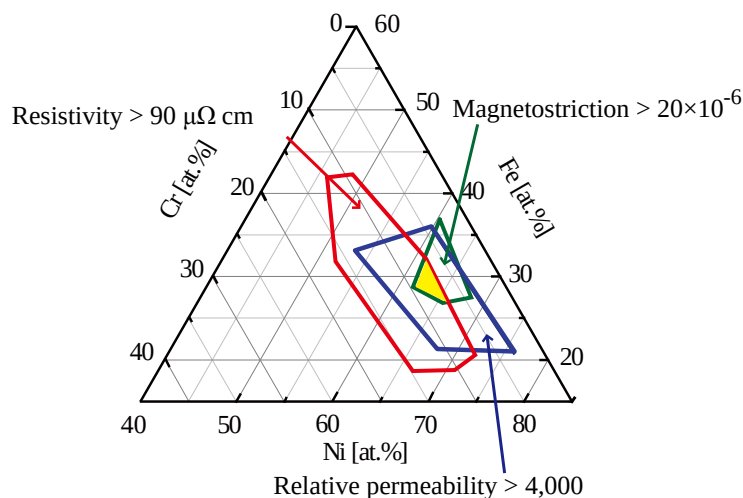


Figure 10. Composition range that satisfies all targeted values (magnetostriction, relative permeability, resistivity)

magnetostriction, and analysis of the results) took three weeks. In contrast, it would take at least 240 days to individually measure the composition, resistivity, relative permeability, and magnetostriction for 240 samples using the same measurement methods described in this paper.

5. Conclusion

Magnetostrictive materials have gained attention due to features such as fast response and high power and could be applied for the conversion of magnetic energy to mechanical energy. Magnetostrictive materials are thus applied for various sensors. However, conventional magnetostrictive materials have not satisfied all of the required properties; therefore, large magnetostriction, high relative permeability and resistivity are required to improve the sensitivity of sensors. In this work, new magnetostrictive materials that have all high properties were searched in the FeNiCr ternary system. Libraries were fabricated by using the Combi-NFTS method to create a composition distribution. The resistivity, relative permeability and magnetostriction were then evaluated by using the four probe method, VSM and deflection of a bilayer cantilever, respectively. The result indicate that the composition range with a Fe content of 26 to 36.5 at.%, a Ni content of 61 to 66 at.%, and a Cr content of 7.5 to 9.5 at.% satisfies all required values. In the future, we expect that these materials will be applied in sensors such as force or displacement sensors.

For the future research, we should investigate the crystallinity, structure, impurity, and morphology of each fabricated samples. Some fabrication process could enhance some properties like other materials (Li, et al., 1993), (Na and Flatau, 2012).

In this paper, the resistivity, relative permeability and magnetostriction were measured individually. The times for the relative permeability and magnetostriction measurements were particularly long, which severely reduced the material searching efficiency. Therefore, in future works, we will apply a microelectromechanical system (MEMS) technique to the simultaneous measurement of the relative permeability and magnetostriction for improvement of the material searching efficiency.

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