Materials Transactions, Vol. 49, No. 3 (2008) pp. 650 to 654

EXPRESS REGULAR ARTICLE

Effects of Alloying Element Balance and Micro-Alloying Elements on Magnetic Properties and Hot Ductility of PC Permalloy

Tadashi Inoue[1], Katsuhisa Yamauchi[1] and Fumio Fujita[2]

[1]*Steel Research Laboratory, JFE Steel Corporation, Fukuyama 721-8510, Japan*
[2]*Department of Materials Science and Engineering School of Engineering, Tohoku University, Sendai 980-8579, Japan*

The present study focused on improving the hot ductility and magnetic properties of PC Permalloy. An alloy with a chemical composition of 78.5 mass%Ni-4.3 mass%Mo-2.2 mass%Cu-0.47 mass%Mn-Fe exhibits the optimum permeability, with μ0.005 of 411,200 and μm of 437,400. The P-value of the alloy was 3.43. Addition of Boron caused undesirable deterioration of magnetic properties, while the effects of Magnesium and Calcium on magnetic properties were small. Mill trials using a 50-ton electric furnace revealed that PC Permalloy with a composition of 78.6 mass%Ni-4.2 mass%Mo-2.1 mass%Cu-0.57 mass%Mn-14 ppmCa-4 ppmS-Fe exhibits extremely high permeability (*i.e.*, μ0.005, 233,000 to 499,000; μm, 368,000 to 568,000). High-permeability alloy sheets were obtained by controlling the P-value in the range of 3.45 to 3.49. The hot ductility of the alloy was markedly improved, and ingots and slabs were hot rolled without any corner cracks.
[doi:10.2320/matertrans.MER2007235]

(Received October 19, 2007; Accepted January 7, 2008; Published February 20, 2008)

Keywords: *PC Permalloy, hot ductility, segregation, grain boundary, boron, sulfur, calcium, magnesium, sulfide. deboronization, magnetic property, permeability, nickel, molybdenum, copper, iron*

1. Introduction

In recent years, measurement technologies using SQUID magnetometers have been developed by industry, universities and governmental agencies and the measurement of very weak magnetic fields generated by living bodies and the precise physical measurement of advanced materials is anticipated.[1,2] These are weak magnetic fields of 10^{-11} to 10^{-14} T (Tesla). However, magnetic field perturbations of 10^{-7} T are generated from moving machines and power supply facilities and are present in urban areas, making measurements using a SQUID magnetometer very difficult in an open space. For this reason, there is a high demand for magnetic shielding technologies that can block magnetic field perturbations and provide a clean magnetic environment.

A magnetic material with high permeability such as PC Permalloy is required for magnetic shielding use in measuring very weak magnetic fields. To make a highly efficient magnetic shielding room using magnetic material with high permeability, wide magnetic material sheet with few joints is required, so a wide PC Permalloy sheet is desired. For these reasons, corner cracks generated during hot rolling due to poor hot ductility of PC Permalloy must be reduced.
Although some studies have investigated how the balance of alloying elements affects the permeability of Ni-Mo-Fe and Ni-Mo-Cu-Fe magnetic alloys to improve the magnetic properties of PC Permalloy,[3–7] further improvement of magnetic properties of PC Permalloy is required to realize highly efficient magnetic shielding. Reduction of impurity elements and addition of micro-alloying elements are important for improving the hot ductility of permalloy,[8–10] but few studies have investigated the effects of these impurity elements and micro-alloying elements on magnetic properties.

This study investigates the fundamental effects of alloying element balance on permeability of PC Permalloy. Investigating the effects of micro-alloying elements that improve hot ductility will contribute to developing PC Permalloy with good hot ductility and excellent magnetic properties.[11,12]

2. Experimental Procedure

The chemical compositions of alloys used in this study are shown in Table 1. The 28 alloys used in this study were all melted in vacuum and cast in 50 kg ingots. The basic chemical composition of alloys No. 1 to No. 9 was Ni-4 mass%Mo-2 mass%Cu-Fe, that of alloys No. 10 to No. 14 was Ni-4 mass%Mo-5 mass%Cu-Fe, and that of Nos. 15 to 23 was Ni-4 mass%Mo-Fe. The P-value was varied by changing the contents of Ni, Fe and Mn. To investigate the effects of Boron, Calcium and Magnesium, alloys No. 24 to No. 26 were prepared with additions of 42 ppm B, 46 ppm Ca and 85 ppm Mg.

The P-value is the ratio of magnetic nickel atoms to iron atoms in complex Ni-Fe alloy as proposed by R. D. Enoch and A. D. Fudge.[6] This theory considers the effect of filling the 3d vacancies of nickel atoms with the outermost electrons of the added non-ferromagnetic elements such as Cu, Mo and Mn. Cu has one outermost electron, Mo has six, and Mn has two.

$$\text{P-value} = \text{magnetic Ni/Fe} = \{C_{Ni}\text{-}1/3\,\Sigma(5Zi\text{-}3)C_i\}/C_{Fe}$$

C_{Ni} : Ni at%, C_{Fe} : Fe at%,
C_i : non-ferromagnetic elements at%
Zi : outermost electrons of non-ferromagnetic elements.
(Zi = 1 for Cu, 6 for Mo, and 2 for Mn)

These ingots were hot rolled to a thickness of 2.5 mm. After de-scaling, hot-rolled sheets were cold-rolled to a thickness of 1.0 mm. Magnetic properties were measured by using ring specimens. The ring specimens were 45 mm

Table 1 Chemical compositions of alloys (mass%).

Alloy No.	Ni	Mo	Cu	Mn	Fe	P-value	Remarks
1	74.9	4.8	2.3	0.83	17.1	2.49	Ni-4 mass%Mo-2 mass%Cu-Fe
2	77.6	4.5	2.2	0.63	15.0	3.16	
3	78.5	4.3	2.2	0.47	14.5	3.43	
4	78.4	3.9	2.8	0.56	14.3	3.58	
5	78.8	4.1	2.0	1.35	13.5	3.62	
6	79.7	4.5	2.2	0.54	12.9	3.84	
7	79.4	4.1	2.1	1.90	12.4	3.89	
8	80.7	4.4	2.2	0.54	12.1	4.21	
9	80.8	4.3	2.1	0.55	12.2	4.25	
10	76.8	4.6	3.6	0.90	14.0	3.18	Ni-4 mass%Mo-5 mass%Cu-Fe
11	76.4	4.0	4.9	0.52	14.1	3.39	
12	76.4	4.2	5.1	0.81	13.4	3.40	
13	76.4	4.0	5.1	0.78	13.7	3.41	
14	76.8	4.2	5.0	0.82	13.1	3.53	
15	80.3	5.6	—	0.45	13.5	3.39	Ni-5 mass%Mo-Fe
16	80.4	5.4	—	0.45	13.6	3.44	
17	80.6	4.5	—	0.72	14.1	3.64	
18	81.5	5.1	—	0.46	12.9	3.87	
19	81.7	5.5	—	0.46	12.2	3.90	
20	81.6	5.5	—	0.74	12.0	3.91	
21	82.2	6.1	—	0.47	11.1	4.05	
22	82.2	5.7	—	0.44	11.6	4.09	
23	82.3	5.6	—	0.46	11.3	4.22	
24	79.6	4.5	2.2	0.54	13.04	3.79	42 ppmB
25	79.7	4.5	2.2	0.54	12.9	3.84	46 ppmCa
26	79.9	4.5	2.2	0.55	12.51	3.97	85 ppmMg

external diameter and 33 mm internal diameter. The ring specimens were annealed for three hours at 1100°C in pure dry hydrogen (dew point less than −40°C) before the magnetic properties were measured. The cooling rate at temperatures from 650°C to 300°C was 89°C/h. The initial relative permeability (μi) at 0.4 A/m and the maximum relative permeability (μm) were measured according to JIS C-2531. The ring specimens were degaussed by applying an AC magnetic field before measuring μi and μm.

Hot ductility was investigated by high-temperature tensile testing. The chemical composition of the alloy used in this study was 78.6 mass%Ni-4.2 mass%Mo-2.1 mass%Cu-0.57 mass%Mn-14 ppmCa-4 ppmS-14.42 mass%Fe. This alloy was melted in a 50-ton electric furnace. High-temperature tensile testing was conducted by using round bar specimens machined from equiaxed grain portions in the ingot and hot-rolled specimens. Testing conditions are shown in Fig. 1. Specimens were heated at 1200°C or 1250°C for 5 minutes, cooled to testing temperature ranging from 900°C to 1100°C, and then deformed at a strain rate of 1 s^{-1}. Zero ductility test was also conducted by the ingot specimens. The hot ductility was evaluated by measuring the reduction area of the fractured portion.

In mill trail, alloy with an optimum chemical composition was melted in a 50-ton electric furnace. Ingots were hot-rolled to slabs by a sizing mill. The slabs were then hot-rolled, cold-rolled, and annealed in Keihin works. Hot ductility of the alloy was evaluated using the ingots. Magnetic properties were measured using ring specimens machined from annealed sheets of the alloy.

3. Results and Discussion

Figure 2 shows the relationship between relative permeability and P-value for alloy No. 1 to No. 23.

The alloy with a P-value of 3.43 (Alloy No. 3) has the highest relative permeability. Ni-Mo-Cu-Fe alloy exhibits higher permeability than Ni-Mo-Fe alloy. This result is consistent with that of R. D. Enoch and A. D. Fudge.[6)]

The alloy with the highest relative permeability was 78.5 mass%Ni-4.3 mass%Mo-2.2 mass%Cu-0.47 mass%Mn-14.5 mass%Fe. The alloy had a P-value of 3.43, which was in good agreement with the result of R. D. Enoch and A. D. Fudge.[6)] We believe that this result is due to domain wall stabilization; the magnitude of the uniaxial anisotropy induced in the domains and domain walls that produces stabilization is related to the Curie temperature of the alloy. The Curie temperature of quaternary alloys is about 50°C lower than those of corresponding ternary alloys so that more stabilization occurs in these alloys.[6)] The 78.5 mass%Ni-

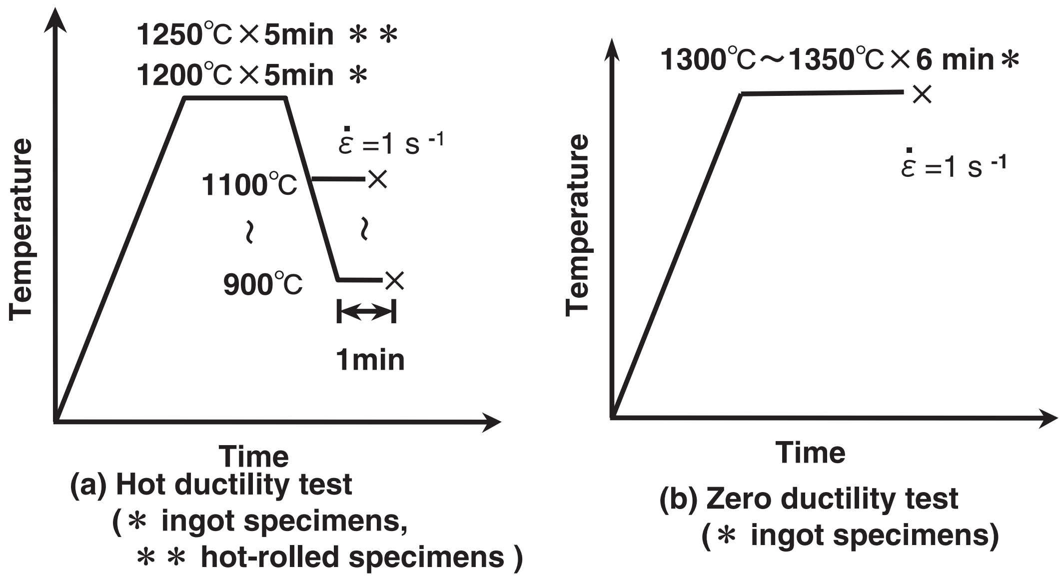

Fig. 1 Schematic view of tensile test and heat cycle.

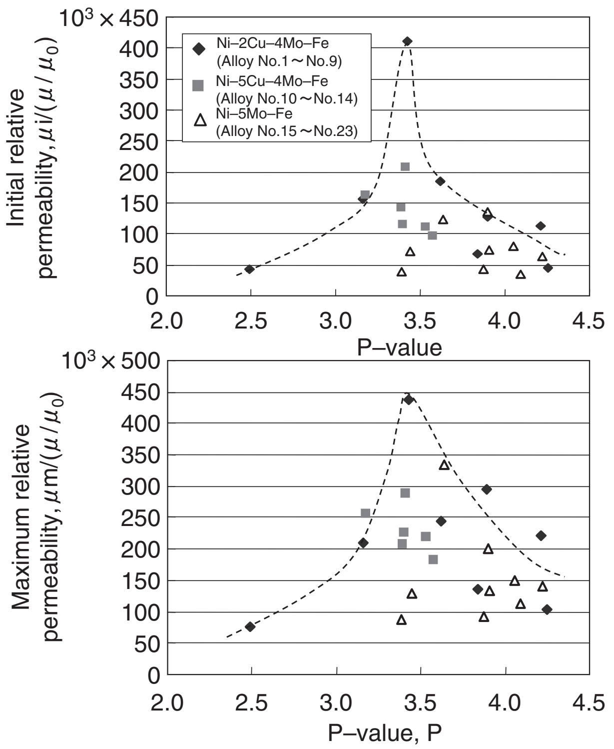

Fig. 2 Relationship between μi, μm and P-value, Annealing condition: 1100°C × 3 h (H2), Cooling rate 650∼300°C: 89°C/h.

4.3 mass%Mo-2.2 mass%Cu-0.47 mass%Mn-Fe alloy exhibits higher relative permeability than 77 mass%Ni-4 mass%-Mo-5 mass%Cu-Fe because the Curie temperature of the former alloy is higher than that of the latter alloy. The former alloy is thus thought to have less long-range ordering which lowers permeability.[6)]

Boron, Magnesium and Calcium improve hot ductility of PC Permalloy.[8)]

Figure 3 depicts the effect of B, Ca and Mg on the relative permeability of PC Permalloy annealed in pure dry hydrogen (alloys No. 24 to No. 26). The relative permeability of alloy

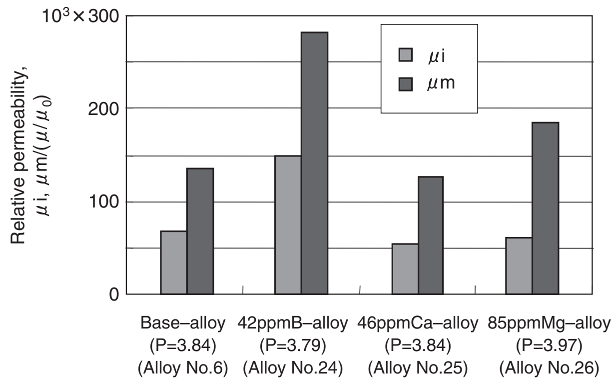

Fig. 3 Effects of B, Ca and Mg on relative permeability of PC Permalloy, Annealing condition: 1100°C × 3 h (H_2), Cooling rate 650∼300°C: 89°C/h.

with B added is higher than that of the base alloy, in which the effects of Ca and Mg on magnetic properties were small.

To examine the effect of B on relative permeability, we investigated the effect of annealing atmosphere on the relative permeability of PC Permalloy containing B melted in a 5-ton vacuum induction furnace. The chemical composition of the alloy was 78.4 mass%Ni-4.3 mass%Mo-2.2 mass%Cu-0.66 mass%Mn-49 ppmB-20 ppmCa-9 ppmS-14.3 mass%Fe. Figure 4 illustrates the effect of annealing atmosphere on the relative permeability of the PC Permalloy. The sample annealed in a higher concentration hydrogen atmosphere exhibited higher permeability than that annealed in a lower concentration hydrogen atmosphere. The sample with high relative permeability also exhibits deboronaization, while the sample annealed in a high vacuum atmosphere (less than 1.33×10^{-2} Pa) possessed the lowest relative permeability and showed less deboronization.

Deboronization in Fe-Ni Alloy is thought to progress in the reaction as follows.[13)]

$$2B + 3/2O_2 \rightarrow B_2O$$

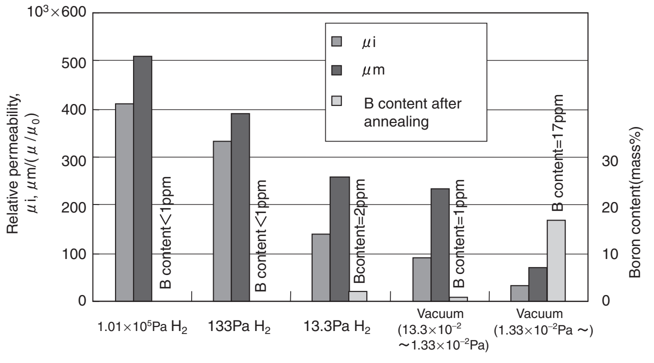

Fig. 4 Effect of annealing atmosphere on relative permeability of the PC Permalloy, 78.4%Ni-4.3%Mo-2.2%Cu-0.66%Mn-49 ppmB-20 ppmCa-9 ppmS-14.3 mass% Fe(P-value: 3.42), Annealing condition: 1100°C × 3 h (H_2), Cooling rate 650∼300°C: 45°C/h.

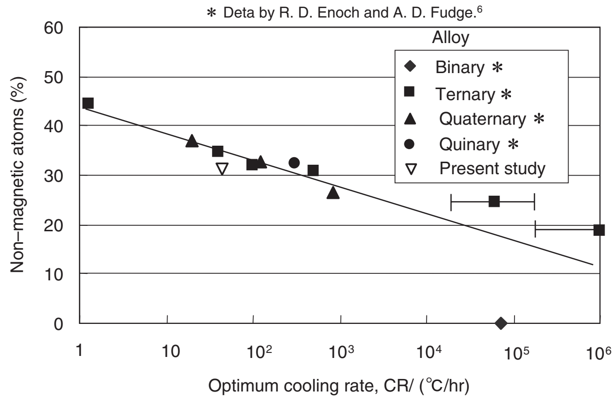

Fig. 6 The percentage of non-magnetic atoms in some optimum complex Ni-Fe alloys plotted against the optimum cooling rate of the alloy.

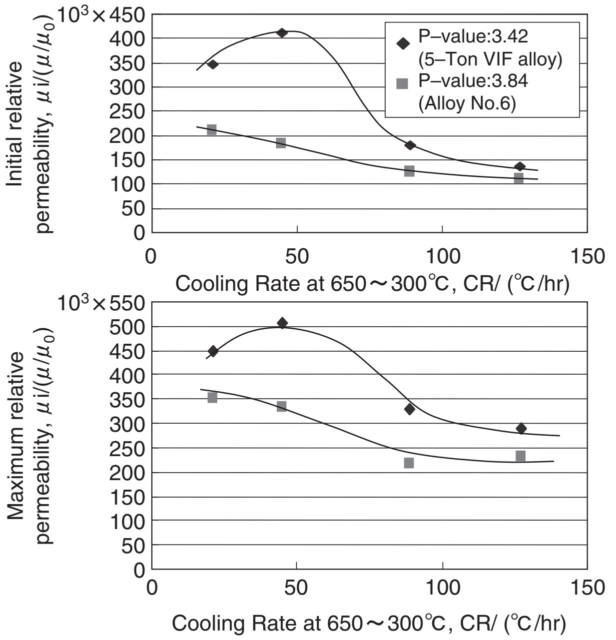

Fig. 5 Effect of cooling rate in the temperature ranges from 650°C to 300°C, annealing condition: 1100°C × 3 h (H_2).

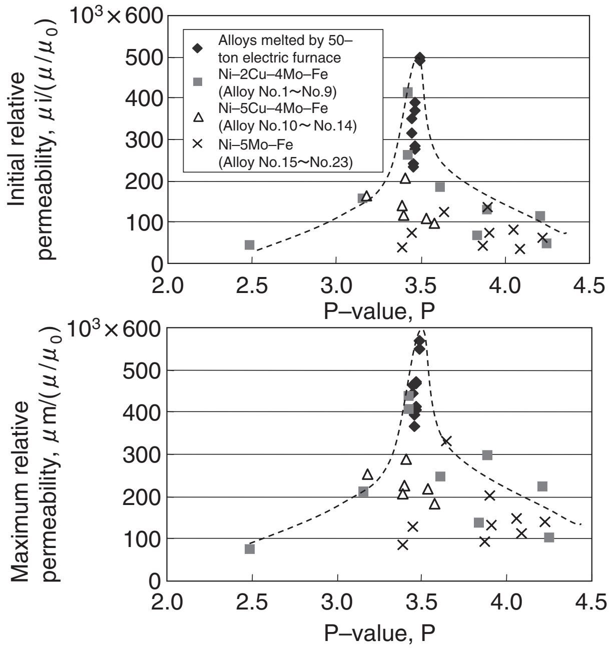

Fig. 7 The relationship between relative permeability of mill trialed alloy and P-value. Annealing condition: 1100°C × 3 h (H2),Cooling rate 650∼300°C: 89°C/h.

We believe that such deboronization affects the magnetic properties of PC Permalloy. Addition of B to PC Permalloy is thought to be undesirable technique for the parts of magnetic shielding room piling up during the annealing process in a lower concentration of hydrogen atmosphere due to the deterioration of the relative permeability from adding B.

Figure 5 plots the effect of cooling rate at temperatures from 650°C to 300°C on relative permeability. The alloy with a P-value of 3.42 has the highest relative permeability permeability at 45°C/h, while the alloy with a P-value of 3.79 exhibits slightly increasing permeability with decreasing cooling rate.

Figure 6 illustrates the exponential relationship between the percentage of non-ferromagnetic atoms present in an alloy and the optimum cooling rate for the alloy by R. D. Enoch and A. D. Fudge.[6)] The optimum cooling rate of an alloy with a P-value of 3.42 in this study is consistent with that of a previous study.[6)] From these results, we consider that the increase of the relative permeability in Ni-Mo-Cu-Fe alloy in this study is attributable to the control of short-range ordering by non-ferromagnetic elements, Cu, Mo, and Mn.

Based on these results, we conducted a mill trial using a 50-ton electric furnace.[11)] The chemical composition of the alloy was 78.6 mass%Ni-4.2 mass%Mo-2.1 mass%Cu-0.57 mass%Mn-14 ppmCa-4 ppmS-14.42 mass%Fe. Ca was added to improve the hot ductility of PC Permalloy without degrading the relative permeability after annealing. Molten metal was cast into seven 7-ton ingots. After sizing, hot-rolling, de-scaling, cold-rolling and annealing, ring specimens machined from these seven coils were annealed in a pure hydrogen atmosphere and magnetic properties were measured.

Figure 7 presents the relative permeability of the mill trial alloy sheets. The P-values ranged from 3.45 to 3.49, μi ranged from 233,000 to 499,000, and μm ranged from

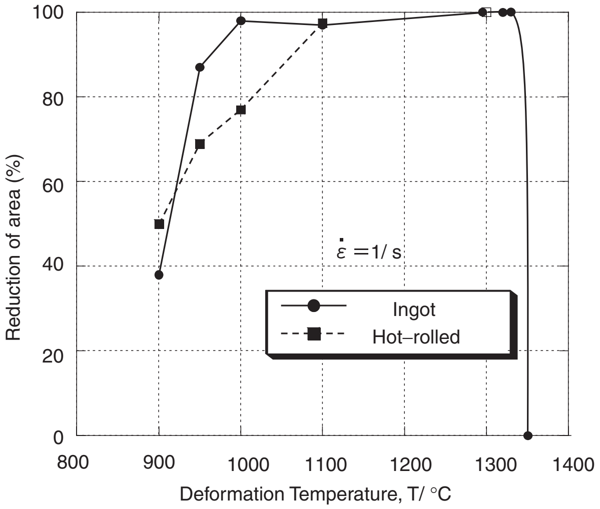

Fig. 8 Hot ductility of the PC Permalloy melted by 50-Ton electric furnace, 78.6%Ni-4.2%Mo-2.1%Cu-0.57%Mn-14 ppmCa-4 ppmS-14.42%Fe.

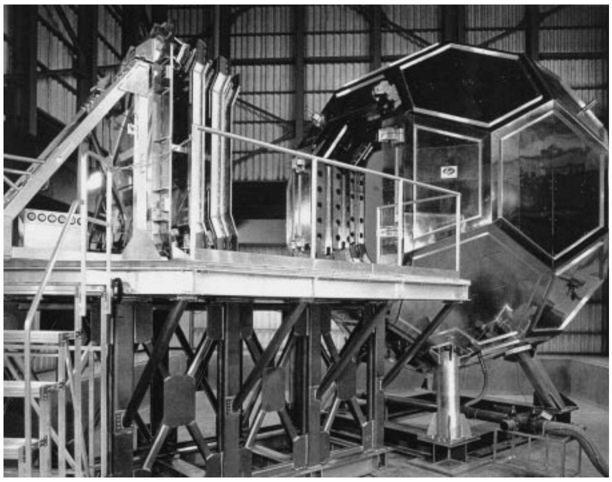

Fig. 9 High performance Magnetically Shield room COSMOS.[11,12]

368,000 to 568,000. High relative permeability alloy sheets were obtained by controlling the P-value in the range of 3.45 to 3.49.

Figure 8 illustrates the hot ductility of the PC Permalloy melted in a 50-ton electric furnace. The hot ductility of the ally was markedly improved, and ingots and slabs were hot-rolled without any corner cracks.

A highly effective magnetically shielded room (COSMOS; Fig. 9) was constructed by Super Conductivity Sensor Lab by applying the developed PC Permalloy sheets.[11,12]

4. Conclusions

The present study focused on improving relative permeability and hot ductility of PC Permalloy. The following results were obtained.

(1) An alloy with a chemical composition of 78.5 mass%-Ni-4.3 mass%Mo-2.2 mass%Cu-0.47 mass%Mn-14.5 mass%Fe exhibits the highest relative permeability, μi: 411,200, μm: 437,400, and the P-value of the alloy was 3.43.

(2) Boron produced undesirable deterioration of the relative permeability, while the effects of Magnesium and Calcium on the relative permeability were small.

(3) Mill trials using a 50-ton electric furnace revealed that PC Permalloy with a composition of 78.6 mass%Ni-4.2 mass%Mo-2.1 mass%Cu-0.57 mass%Mn-14 ppmCa-4 ppmS-14.42 mass%Fe has extremely high relative permeability (*i.e.*, μ0.005, 233,000 to 499,000, and μm 368,000 to 568,000. High-permeability alloy sheets were obtained by controlling the P-value in the range of 3.45 to 3.49. The hot ductility of the alloy was markedly improved, and ingots and slabs were hot-rolled without any corner cracks.

Acknowledgements

The authors wish to thank Dr. T. Okita for helpful suggestions and comments. The assistance of other colleagues is also appreciated. The photograph in this paper is used with permission of the Super Conductivity Sensor Lab.

REFERENCES

1) K. Hamazaki and T. Yamashita: Transaction of the Institute of Electronics, Information and communication Engenneers **73** (1990) 947.
2) K. Niki, T. Inoue and M. Nakagawa: NKK Technical Review **70** (1994) 16.
3) R. M. Bozoroth: *Ferromagnetism* (New York: Van Nostrand, 1951).
4) G. Rassmann and U. Hofmann: J. Appl. Phys. **39** (1968) 603.
5) G. Y. Chin: Trans. IEEE Mag. **MAG-7** (1971) 102.
6) R. D. Enoch and A. D. Fudge: Brit. J. Appl. Phys. **17** (1966) 623.
7) T. Kato, T. Takano and S. Yahagi: Denki Seiko **48** (1977) 265.
8) T. Inoue, K. Fujita, K. Yamauchi and Y. Hosoya: Tetsu-to-Hagane **89** (2003) 848.
9) M. Tsuda and R. Nemoto: Tetsu-to-Hagane **80** (1994) 729.
10) S. Yamaguchi, H. Kobayashi, T. Matsumiya and S. Hayami: Metals Technology May (1979) 170.
11) K. Yamauchi, S. Okimoto, T. Inoue, K. Matsumoto and O. Suzuki: Materia. Jpn. **34** (1995) 652.
12) K. Harakawa, A. Kajihara, K. Kazami, H. Ogata and H. Gato: Tec. Soc. Report of the Institute of Electrical Engineers of Japan (IM-94-37) (1994) pp. 17–24.
13) M. Tsuda: Tetsu-to-Hagane **82** (1996) 153.