Magnetic and Electrical Properties of Rapidly Quenched Nickel and Manganese Alloy Ribbon

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Yasumasa YAMASHIRO*, Kenji NARITA**

Abstract—Ni_3Mn alloy has the Cu_3Au type crystal structure and its magnetic properties deeply depend on the degree of its order-disorder transformation. It takes, however, a considerably long time to make order-disorder transformation occur. The alloy, named nimalloy, has been forged into a thin ribbon by using a new fabricating method that is called "Rapidly Quenching Method". It has been discoverd that the ribbon, fabricated by this method, shows a ferromagnetic characteristic after being annealed for one hour under the order-disorder transformation temperature. And it has been found that the saturation magnetic flux density and coercive force vary according to Mn composition. The former reaches 4 KG at 22 at% Mn; the latter varies from 35 to 90 Oe. The ribbon has a specific electrical resistivity of 61.7~87.5 $\mu\Omega$-cm at room temperature and tensile strength of 76.0 kg/mm^2.

I. Introduction

Ni_3Mn alloy has Cu_3Au type crystal structure[1]. It is face-centerd cubic lattice in the disorderd state; on the other hand, when it is orderd, Ni occupies face-center position and Mn occupies body-center position. Because this alloy has a close relationship between the ordering and magnetic properties, a large number of studies[2)~9)] have been carried out on the phase diagrams of nickel-manganese alloy since Zemczuzny et al. began their work in 1908. These results have extended over many fields. Kaya and Kussmann[3] were the first investigaters who measured in greater detail the variation of magnetic and electrical properties of nickel alloys containing 15~40% manganese after various heat treatment. They discovered that these alloys are ferromagnetic in ordered state, although they are paramagnetic in disordered state. They explained ferromagnetic supperlattice of Ni_3Mn would be formed in the nickel-manganese alloy…either by slow cooling from a high temperature or by heating for a long time below 500°c after rapid cooling. The order-disorder transformation temperature of Ni_3Mn extends from 300°c to 600°c, as shown in Fig. 1[4]. Due to this fact, it is considered that the way of growing the ordered phase varies according to the heat treatment temperature. Marcinkowski et al.[5] showed that the process of growing the ordered phase is complicated, and summarized as follows: (1) long-range order (LRO) occurs uniformly when the heat treatment temperature is below 425°c; the ordering speed, however, is very slow; as is evident in the example, it takes thousands of hours at 420°c to

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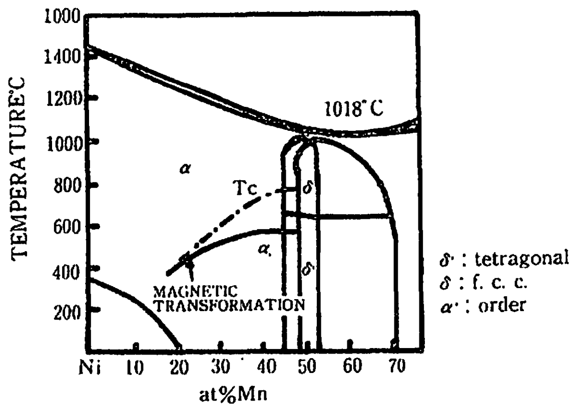


Fig. 1 Phase diagram of Ni-Mn alloys system[4]

make the ordered phase in the whole sample, (2) with the constant heat treatment at 425°c ~480°c, short-range order (SRO) appears at first; thereafter, (LRO) deposits in (SRO) mosaicaly but does not extend to the whole region, even if it is annealed for a long time, (3) (SRO) grows uniformly when the heat treatment temperature is over 480°c. Yokoyama et al.[1] forecasted the possibility that the alloy is able to have high magnetic permeability in (1) state, but the hysteresis loop was similar to a permanent magnet's one in (2) state. This was in accord with the differences of the heat treatment temperatures though they are the same alloys and have the same compositions. The hysteresis loop was measured, and Yokoyama et al. observed the magnetic domain structures after being annealed at constant temperature of 420°c and 470°c.

As for magnetic permeability, Jaffee[6] obtained an initial permeability of 5, 300 in a Ni_3 Mn alloy heated at 380°c for a long time. Y. Murakami[7] obtained an initial permeability of 24,500 and a maximum permeability of 98,000 in a nickel alloy containing 24% manganese, by a slow cooling from the order-disorder transformation temperature or by reheating it again under the same temperature after it is made homogeneous in high pure H_2 gas. Masumoto et al.[8] obtained the highest initial permeability of 6,860 in an alloy containing 21.91% manganese when heated at 380°c for 50 hours after cooling at a rate of 10°c/hr. from 900°c; an alloy with the composition of 22.0% manganese attains the highest maximum permeability of 20,400 when heat-treated similarly. The former has a coercive force of 0.031 Oe and a specific electrical resistivity of 60.7 $\mu\Omega$-cm at 20°c. In further studies[9] they obtained the highest initial permeability of 76,000 and the highest maximum permeability of 441,000 in the Ni-Mn-Fe-Cr system; on the contrary, in the Ni-Mn-Ge system, the highest initial permeability of 151,800 and the highest maximum permeability of 167,000 were obtained. They are much higher than those of silicon iron steel or 78% nickel iron alloy. Moreover, they indicated that nimalloy has a small hysteresis loss, whereas the $4\pi I$ and permeability are also small. They showed that nimalloy with-composition 23.24% manganese has a high coercive force, but the alloy is perminver type because the mixture of (LRO) and (SRO) exists. As discovered above, the nickel-manganese alloy has various peculiar characteristics according to its composition: either high permebility and low hysteresis loss, or high coercive force. But it takes a long time to make the ferromagnetic superlattice occur and grow in the alloy, therefor, it has not been used yet industrially and commercially in spite of good magnetic and electrical properties. The alloy is expected to be realized as an industrial magnetic material if the heat treatment time could be shortend.

It is considered that there are the the following ways in developing new materials : (1) progressing the former studies, (2) making a new alloy, (3) developing a new fabricating method. Some reports[10~13] have been already published on a new metal filament and ribbon fabricating method, named "Rapidly-Quenching method (RQM)". The authors tried to apply (RQM) to forge the nimalloy ribbon[14,15] in order to sherten and stabilize the order - disorder transformation time. As a result, we have got a ferromagnetic alloy after annealing the rapidly - quenched nimalloy ribbons for only one hour in a vaccum.

II. Sample Preparation and Experimental Apparatus

There are two methods in (RQM)[16] which are introduced to make metal filament and ribbon; one is disk method, the oter is roll method. This is a method where molten metal is jet-ejectjd onto a roller's surface, which is rotating with high speed, and afterwards rapidly quenched. This roll method is further divided into two ways: single - roll method and twin - roll method. We have adopted here the former because it is simpler to operate[17]. The brief schematic view of apparatus for fabricating samples is illustrated in Fig.2. Electrolytic nickel and electrolytic manganese, of which purities are over 99.9%, were used as raw materials,

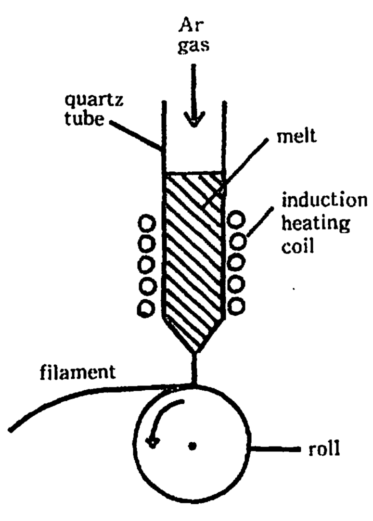


Fig. 2 Apparatus for fabricating ribbons

Table 1. Condition of fabricating ribbons

Name	Single-roll method
Diameter of roll	120mm
Surface velocity	35 m/sec
Diameter of nozzle	0.5~0.6mm
Ar gas pressure	0.5Kg/mm²

Table 2. Shape of fabricated ribbons

Thickness	20~30 μm
Width	1~2mm
Length	various

and they were put in a quartz tube with an inside diameter of 5 mm and a nozzle's diameter of 0.5~0.6 mm The nozzle was located the bottom of the tube. The bottom with nickel and manganese was heated by high frequency induction until the materials were melted in Ar gas atmosphere. The quartz tube was succesively pushed down by Ar gas piston to a position which was very close to the roll surface that was rotating with consistent high speed. Immediately, the melted alloy was jet - ejected onto the roll surface and was rapidly quenched. The roll was made of stainless steel and was 120 mm in diameter. The condition of fabricating nimalloy ribbon is tabulated in Table 1. The sizes of ribbons thus fabricated were 20~30 μm in thickness, 1 ~ 2 mm in width and several meters in length. The thickness and width were measured with a micrometer. The dimension of ribbons fabricated by this methoed is shown in Table 2. Those ribbons were silver white, very flexible and easily wound into troidal shape with a 1 mm diameter. This is quite the same methd in which amorphous materials are fabricated. However, the fabricated ribbons were in a crystalline state. The shape of the ribbons and the thickness depended on the melting temperature, roll speed, diameter of the nozzle and Ar gas jet - pressure. Generally, when the melting temperature was high or the rotation number of the roll was large, the melted alloy was spread out like a fire - ball. However, the tendency was also observed that the oxidization of the ribbons' surface proceeded because the cooling effect of the roll was inadequate. In contrast, when the melting temperature was low, the issue of melted alloy out of the nozzle was disturbed, moreover, no ribbon with a good surface could be produced because the nozzle was blocked by the molten alloy. When the number of roll rotation was too small, the roll surface was deeply wounded, therefore it was very difficult to produce a good surfaced ribbons. Besides, the fabricating condition of nimalloy ribbons was much more difficult and severer than that of the amorphous materials or metallic materials, like the silicon iron.

In order to induce the ferromagnetic characteristic with superlattice Ni_3Mn in thus prepared ribbon, it was annealed in an electric furnace in a vaccume for one hour at 500°C anc 700°C, and following that, it was furnace-cooled.

The magnetic flux density and coercive force were evaluated from DC hysteresis loop of magnetic moment vs. DC field which was measured with high sensitive Vibrating-Sample -Magnetometer. The method by which saturation magnetic flux density Bs was caluculated is shown in Fig. 3. The sample hysteresis loop is one of 25 at% Mn. As shown in the figure, the loop appears as if paramagnetism was superimposed on ferromagnetism. Therefore, a tangent which touches the curve at point P, where ferromagnetism seems to disappear; is drawn and an intersection Q between the extention of the tangent and vertical axis is obtained. Bs is caluculated from the length on the vertical axis OQ by appling the geometrical relationship between magnetic moment M and Bs. The tensile strength was measured with a simple apparatus, as shown in Fig. 4, which was made by ourselves. The cross section of samples was derived from their weight measured with microbalance, length measured with longitudinal ruler and density calculated from the alloy's composition. And all measurements were carried out at room temperature.

Furthermore, we observed the samples' surfaces with an optical microscope so that we could examine the dependence of every physical property on grain structure. The samples for observation were prepared as follows: samples were chemically corroded after having polished with polishing papers, then they were electrolytically polished in a phosphoric acid solution with 10% chromium trioxide.

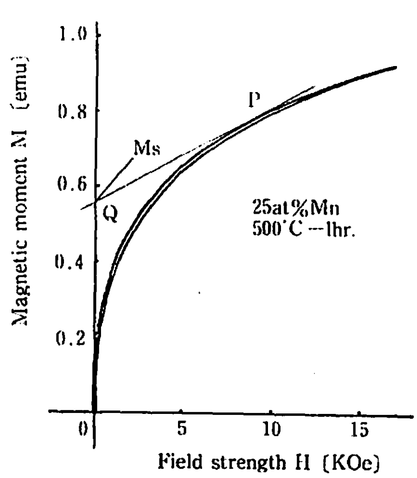


Fig. 3 Schematic explanation of the method of calculating saturation flux density Bs

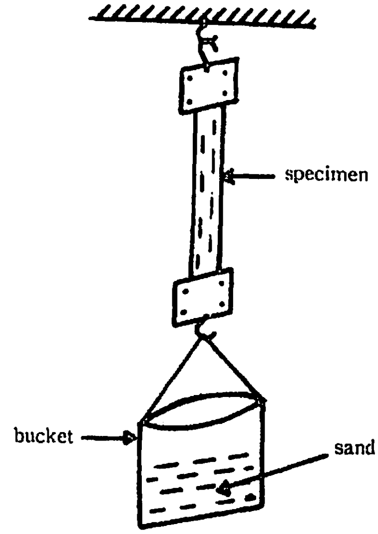


Fig. 4 Apparatus for tensile strength measurement

III. Experimental Results and Considerations

The results of measurements are given in Fig. 5~10, Table 3~4 and Photo. 1. Fig. 5 shows the annealing effect on the magnetic characteristic of 25 at% Mn. As shown in the figure, the ribbon reveals a ferromagnetic property to some extent; the value of Bs is 1.4 KG after it was annealed at 500°C for one hour in a vaccum. Meanwhile it demonstrates only a slight one ---the value of Bs is merely 0.13 KG when annealed at 700°C, and it is quite paramagnetic as it is prepared. It is considered that magnetization has become small in case of the 700°C-1hr. heat treatment because the Curie point falls near room temperature as well as bulk nimalloy. The measurement result of tensile strength is shown in Table 3. Nimalloy ribbon's tensile strength is about twice the value of the bulk's strength, in both cases of as -grown and 500°C-1hr. heat treatment. On the other hand, the value decreases by about 60% in the 700°C-1hr. case. For this reason, we prepared the samples by annealing at 500°C-1hr. in a vaccum in order to examine the magnetic and electrical properties' dependence on Mn content. Those measurement curves are shown in Fig. 5 and Fig. 6 (a)~(e). Those curves

Table 3. Dependence of tensile strength of Ni-Mn ribbons on heat treat ment

As grown	76.8Kg/mm²
500°C-1 hr.	76.0
700°C-1 hr.	42.1

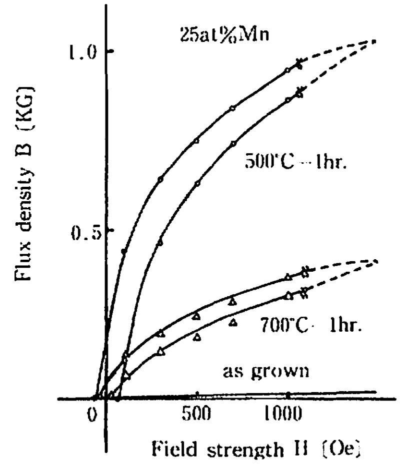


Fig. 5 Effect of heat treatment

were drawn at the magnetic field under 2 KOe after the 15 KOe field was supplied. Judging from them, the magnetic properties strongly depend on Mn content. The rising of the magnetic characteristic curve becomes steeper and steeper till it reaches 22 at% Mn, after which point the curve decreases again gradually. (We call your attention to the scale difference of the vertical axis.)

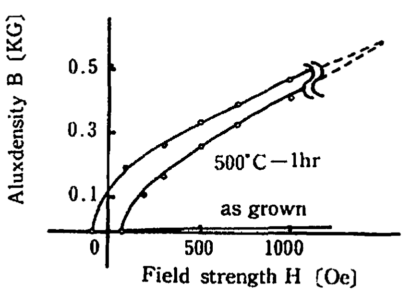


Fig. 6 (a) 20 at % Mn

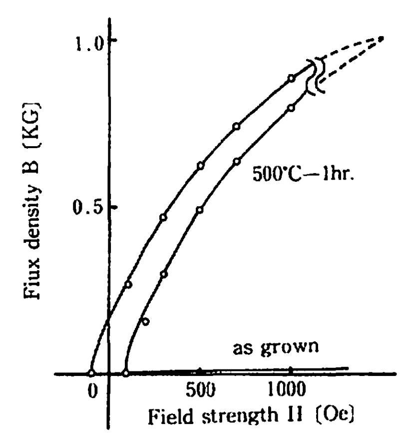


Fig. 6 (b) 21 at% Mn

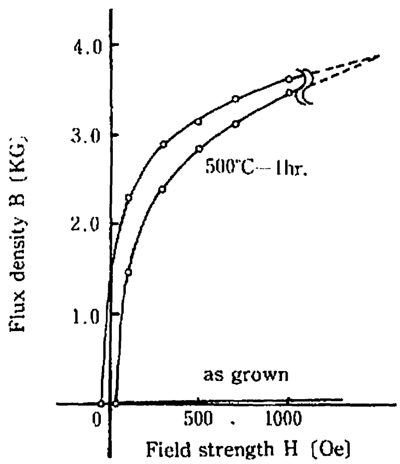


Fig. 6 (c) 22 at% Mn

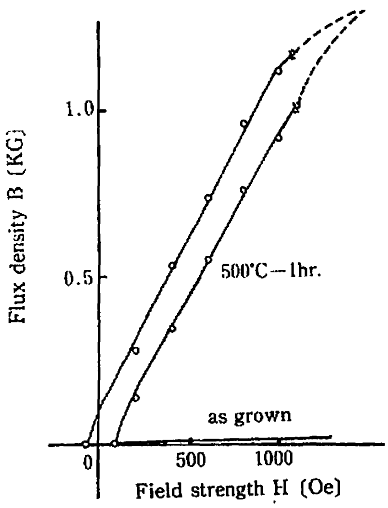
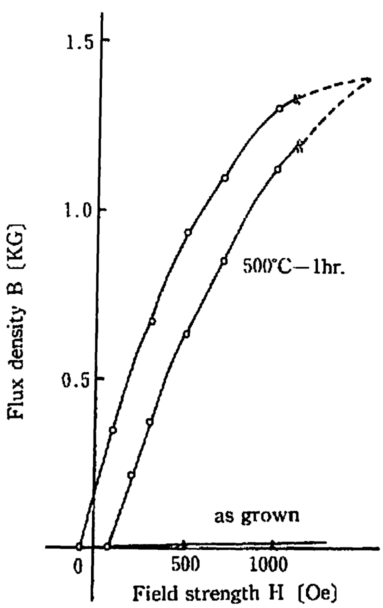


Fig. 6 (d) 23 at% Mn



(e) 24at%Mn.

Fig. 6 Hysteresis loops of Ni-Mn alloys' ribbons

Fig. 7 shows Bs dependence on Mn content, which is caluculated from Fig. 5 and Fig. 6. In the Fig. 8 the magnetic induction at field strengh of H = 15 KOe is shown in both the case of as-grown sample and annealed sample. It is obvious from those figures that formation of Ni_3Mn superlattice depends strongly on Mn content and heat treatment. Bs increases rapidly as increasing Mn content untill 22 at% Mn and then decreases after passing through the maximum, and it reaches even 4 KG at 22 at% Mn. On the ther hand, it is about 3 KG in bulk nimalloy.

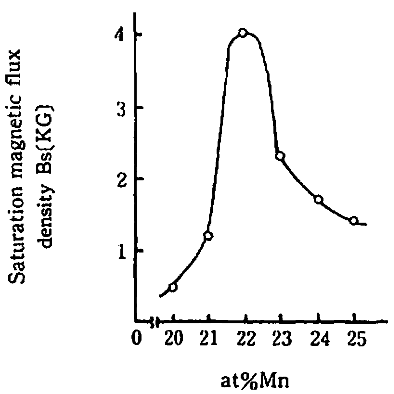


Fig. 7 Dependence of magnetic Flux density at 15 (Koe) field on Mn content in Ni-Mn alloys' ribbons

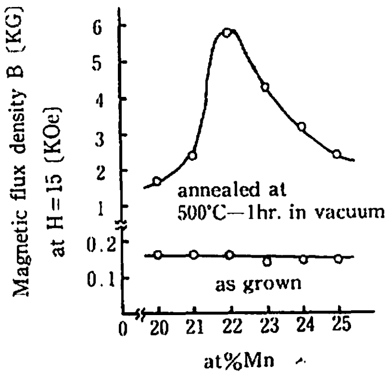


Fig. 8 Dependence of saturation magnetic flux densities on Mn content in Ni-Mn alloys' ribbons after annealed at 500°C for one hour in vaccum

Fig.9 shows the dependence of the coercive force Hc on Mn content. Hc varies according to Mn content similarly to the variation of Bs, and it thows one minimum of 35 Oe and two maxima··· 90 and 80 Oe, which are much larger than that of bulk nimalloy.

Fig.10 shows the electrical resistivity dependence on Mn content. It seems that resistivity is almost constantly independent of Mn content, tendency of the curve is quite similar for the as - grown sample and annealed one. The value of electrical resistivity is about 65 $\mu\Omega$ - cm. It is a little lager than that of bulk nimalloy of 60.7 $\mu\Omega$ - cm, so that we may expect eddy current loss to become smaller in the ribbon than in the bulk.

In the Photo.1, grain structure's pictures of as - grown and 500°c - 1hr. heat treatment samples are in cases of 20, 22 and 25 at% Mn respectively. They show that grain size is 10 ~25μm in 20 at% Mn, and 5~15 μm in 22 and 25 at% Mn as it is grown. Meanwhile they decreases one half size after being heat - treated in every Mn content. This result coincides with the fact that electrical resistivity does not vary so much to Mn content, and that tensile strength does not vary, either before or after heat treatment. Therfore, We may regard that the ferromagneticity of nimalloy ribbons is principally due to ferromagnetic superlattice formation rather than grain growth.

Every magnetic and electrical property is tabulated in Table4.

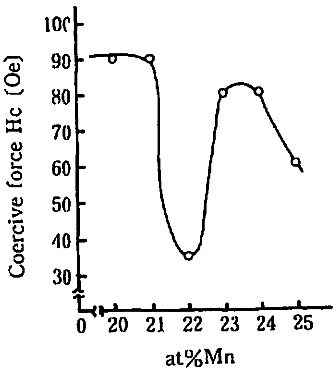


Fig. 9 Dependence of coercive force on Mn content in Ni-Mn alloys' ribbons after beeing annealed at 500°C for one hour in vaccum

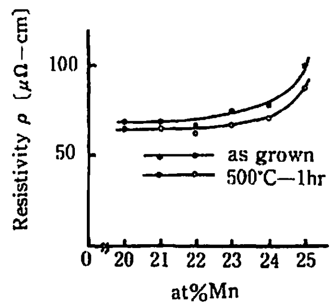
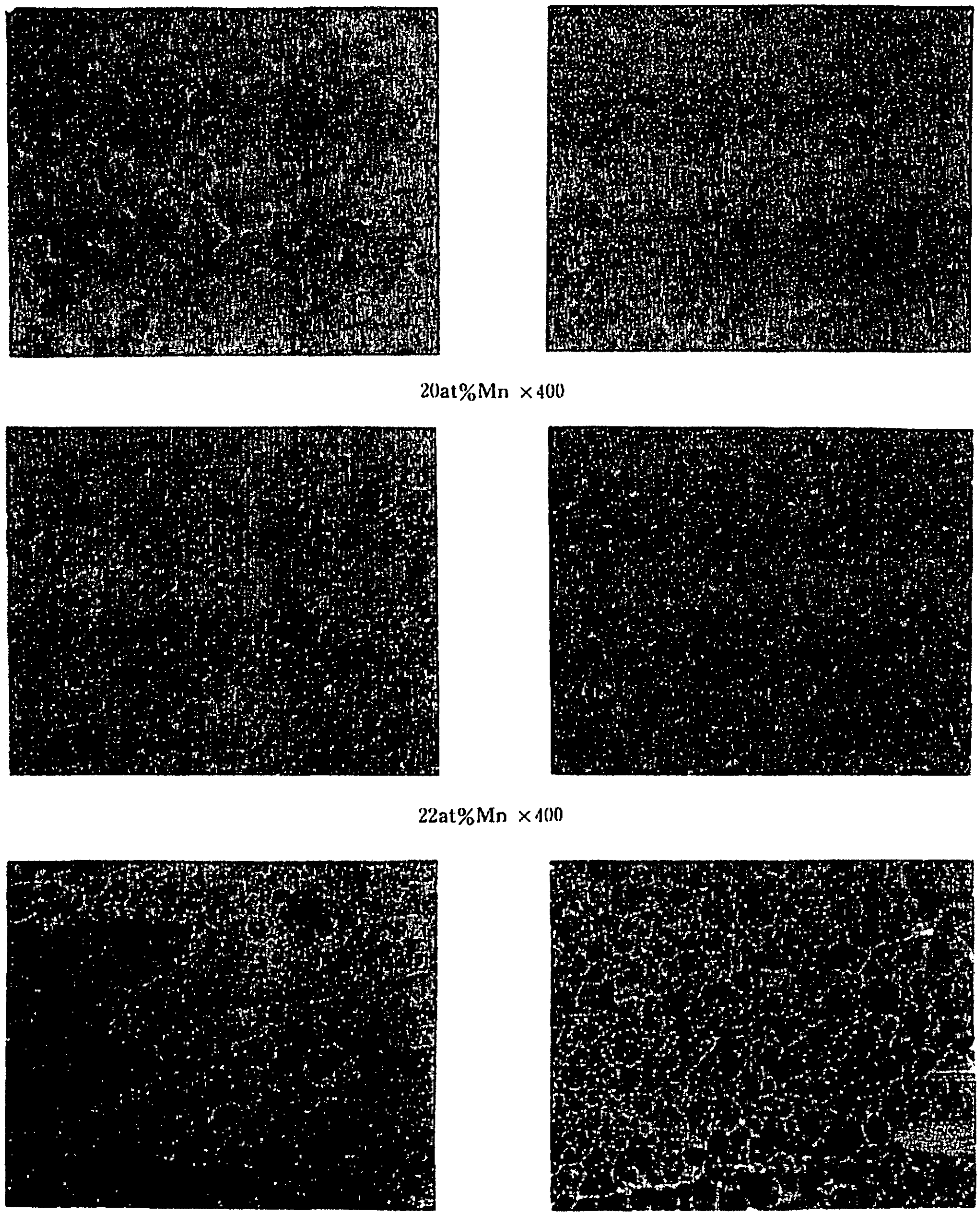


Fig. 10 Dependence of resistivity on Mn content in Ni-Mn Alloys' ribbons

Table 4. Magnetic and electrical properties of Ni-Mn ribbons

Specimens Mn at%	Resistivity ρ (μΩ-cm) as grown	Resistivity ρ (μΩ-cm) 500°c-lhr.	Flux density B(KG)(H = 15KOe) as grown	Flux density B(KG)(H = 15KOe) 500°c-lhr.	Coercive force Hc(Oe)	Saturation flux density Bs(KG)
20	68.4	65.0	0.16	1.7	90.0	0.5
21	68.6	66.6	0.16	2.4	90.0	1.2
22	66.0	61.7	0.16	5.7	35.0	4.0
23	74.5	66.6	0.14	4.3	80.0	2.3
24	78.5	70.0	0.15	3.2	80.0	1.7
25	100.4	87.5	0.15	2.4	60.0	1.4



20at%Mn ×400

22at%Mn ×400

25at%Mn ×400

(a) as grown (b) 500°C—1hr.

Photo. 1 Grain structures of Nimalloy ribbons with various manganese content, and annealing effect on them

IV. Summary

Nimalloy ribbons were fabricated by single - roll rapidly - quenching method and they were heat - treated for one hour in a vaccume at 500°c which is in the region of order - disorder transformation temperature. Magnetic and electrical properties were measured at room temperature, with the results summarized as follows:

(1) The ribbon shows ferromagnetic characteristic after being annealed for only one hour.

(2) Saturation magnetic flux density Bs increases rapidly with increasing manganese content and then decreases gradually after passing through the maximum.
The largest value of Bs is 4 KG at 22 at% Mn.

(3) Coercive force Hc decreases rapidly with increasing manganese content. Then the coercive force increases rapidly after passing through the minimum to reach the second maximum, after that it derreases again gradually. The lowest value of Hc is 35 Oe and the highest is 90 Oe.

(4) Electrical resistivity is almost constant without being affected by the manganese content, and the value is about 65 $\mu\Omega$ - cm.

(5) Tensile strength is fairly large (76.0 kg/mm²) ; in addition it can be wound readily into troidal core of 1 mm in diameter and manufactured easily.

(6) Heat treatment for one hour practically does not make the grain size change. The magnetic domain was not observed, though the ribbon showed ferromagnetic characteristic.

Acknowledgement

We are pleased to acknowledge the considerable assistance and helpful advice of Mr. Teshima of Kyushu University. Mr.Maeda, Sunagawa and Senaha, who graduated from the Department of Electrical Engineering of Ryukyu University in 1980, Mr.Fukuda and Suruhara, who graduated in 1981, should be gratefully appreciated for assistance in measurement.

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